Trigonal Prismatic vs Octahedral Coordination Geometry: Syntheses and Structural Characterization of Hexakis(arylthiolato) Zirconate Complexes

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Treating $[Li(tmeda)]_2[Zr(CH_3)_6]$ with aryl thiols, HSC_6H_4-4-R, in a 1:6 stoichiometry in diethyl ether affords excellent yields of $[Li(tmeda)]_2[Zr(SC_6H_4\text{-4-R})_6]$, where R = CH_3 ($\mathbf{1}^{2-}$) or OCH_3 ($\mathbf{2}^{2-}$) and tmeda denotes *N*,*N*,*N*′,*N*′-tetramethylethylenediamine. These complexes are air-sensitive canary-yellow solids, soluble in hexane, diethyl ether, THF, and acetonitrile, that form yellow single crystals of $[Li(tmeda)]_2\mathbf{1}$ (diethyl ether solution) or $[Li(THF)_3]_2\mathbf{2}$ (THF solution) from saturated solutions at −20 °C. Both complexes were characterized by X-ray crystallography and consist of a zirconium atom coordinated solely by the sulfur atoms of six aryl thiolate ligands in a nonoctahedral geometry. In each structure the lithium cation coordinates to the three sulfur atoms on the triangular faces of the S_6 pseudotrigonal prism. These lithium−sulfur interactions appear to play a role in determining the coordination geometry about the metal center by orienting the sulfur lone pairs of electrons slightly out of the plane defined by the S_3 triangular face and tilted away from the zirconium atoms. A likely consequence is the positioning of the sulfur lone pairs of electrons away from orthogonality with the zirconium−sulfur vector, and hence, they are poorly arranged to π-interact with zirconium. Complex $\mathbf{1}^{2-}$ with a twist angle of ca. 9.18° (trigonal prism, 0°; octahedron, 60°) agrees with the interpretations of computational studies on d^0 complexes, which suggest that a nearly trigonal prismatic geometry is favored when the interaction between metal and ligand is primarily through σ-bonds. The intrinsically weak π-donor thiolate ligand is probably converted to a primarily σ-bonding system by the lithium−sulfur interaction. On the other hand complex $\mathbf{2}^{2-}$ with a twist angle of ca. 30.38° is trigonally twisted to the midpoint of the trigonal prismatic-to-octahedral reaction coordinate. In complex $\mathbf{2}^{2-}$ the 4-OCH_3 group is an electron donor by resonance effects that possibly may lead to the movement away from the expected trigonal prismatic geometry due to either π-interactions or electrostatics repulsion.

Introduction

A classic question of transition metal coordination chemistry concerns the nonoctahedral geometry in [M(dithiolene)$_3$] complexes.[1] While the MS_6 core in several metal d^0 trisbidentate thiolate complexes distorts from octahedral geometry along a C_2 axis,[2] the majority of structurally characterized complexes twists toward the trigonal prismatic limit.[1,3] Stabilization of the MS_6 trigonal prismatic geometry has been attributed to several factors such as charge on the donor atoms, ligand constraints, and metal ligand π-bonding interactions.[3d] Theoretical studies have provided several controversial interpretations.[4] Recently, interest related to the interplay of parameters effecting deviations from octahedral geometry has gained momentum since the publication[5] of $[Zr(CH_3)_6]^{2-}$, the first example of a nearly trigonal prismatic d^0 ML_6 complex possessing monodentate ligands. Current computational studies on hexaorgano and hexahydrido complexes of transition metals agree that the coordination sphere of many d^0 ML_6 complexes favors a geometry close to the trigonal prismatic limit (C_{3v} or D_{3h}) in the absence of steric or π-bonding effects.[6] Over the past few years this postulate has been well supported by the structural determinations of distorted trigonal prismatic hexaorgano complexes: $[Ta(C_6H_4\text{-4-R})_6]^-$ (R = H, CH_3);[7] $[M(CH_3)_6]^{z-}$ (M, z = Ta, 1; Nb, 1; W, 0);[8] and the more complex system[9]

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$[Ta(C{\equiv}CSi^{t}Bu_3)_6]^-$. Extension of this line of research to homoleptic complexes containing ligand donor atoms other than carbon has been little discussed.[10]

Presently, the number of complexes containing a near-trigonal prismatic coordinated metal center is still small, and more experimental data, particularly those containing donor atoms other than carbon, would provide insights valuable to researchers actively refining bonding theories. Recently, we reported complexes containing monodentate thiolate ligands, $[NH_2(CH_3)_2][Ti_2(SCH_3)_9]$ and $[Ti_3(SCH_3)_{12}]$, exhibiting large trigonal twists from the octahedral limit.[11] To further explore this phenomenon, we employed the novel treatment of $[Zr(CH_3)_6]^{2-}$ with aryl thiols (1:6) in diethyl ether that afforded excellent yields of $[Zr(SC_6H_4\text{-}4\text{-}R)_6]^{2-}$. We report here the syntheses and structural characterizations of $[Li(tmeda)]_2[Zr(SC_6H_4\text{-}4\text{-}CH_3)_6]$ ($[Li(tmeda)]_2$**1**, where tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) and $[Li(THF)_3]_2[Zr(SC_6H_4\text{-}4\text{-}OCH_3)_6]$ ($[Li(THF)_3]_2$**2**). The X-ray structure analyses show a nearly trigonal prismatic ZrS_6 core in $\mathbf{1}^{2-}$, while in $\mathbf{2}^{2-}$ the core is twisted to the midpoint of the trigonal prismatic-to-octahedral reaction coordinate. Compound $[Li(tmeda)]_2$**1** represents the first homoleptic monodentate thiolate complex of zirconium unambiguously determined to contain a nearly trigonal prismatic central core. In addition to providing information on a poorly represented class of compounds, $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ provide an approach for studying the influence of heteroatom ligands on the coordination geometry of the central d^0 metal atom. While the deconvolution of the factors involved in determining metal coordination geometry is a complex multivariable problem, the ability to modify the aryl group may provide new insights as more examples of homoleptic monodentate thiolate complexes of zirconium emerge.

Experimental Section

Chemicals and Instrumentations. All reagents were newly purchased from commercial sources and used without further purification except where noted. A literature procedure[5] was used to prepare $[Li(tmeda)]_2[Zr(CH_3)_6]$. Diethyl ether and THF solvents were procured from Fisher and distilled from Na-benzophenone. Zirconium tetrachloride, $HSC_6H_4\text{-}4\text{-}CH_3$, $HSC_6H_4\text{-}4\text{-}OCH_3$, 1.4 M methyllithium, d_3-acetonitrile, and *d*-chloroform were purchased from Aldrich. Proton, ^{13}C, $^{13}C\{APT\}$, and correlation spectroscopy (COSY) NMR spectra were obtained using a Varian VXR-400 FT-NMR. Melting points were measured on a Thomas-Hoover melting point apparatus and are uncorrected. Elemental analyses were carried out with a Perkin-Elmer CHN elemental analyzer 2400. All experimental work was performed under an inert atmosphere using deoxygenated solvents if not otherwise mentioned.

$[Li(tmeda)]_2[Zr(SC_6H_4\text{-}4\text{-}CH_3)_6]$. A pale-yellow solution of $HSC_6H_4\text{-}4\text{-}CH_3$ (1.724 g, 13.9 mmol) in diethyl ether (5 mL) was added dropwise to a slurry of $[Li(tmeda)]_2[Zr(CH_3)_6]$ (0.977 g, 2.3 mmol) in diethyl ether (7 mL) at −78 °C. Immediately, gas evolution occurred and a thick yellow precipitate developed. The yellow slurry was stirred for 20 min at −78 °C and then for 2 h at 21 °C. The reaction mixture was stored for 2 days at −15 °C. The liquid was drained, and volatiles were removed in vacuo to yield $[Li(tmeda)]_2[Zr(SC_6H_4\text{-}4\text{-}CH_3)_6]$ (2.15 g 2.0 mol, 86% based on $[Li(tmeda)]_2[Zr(CH_3)_6]$) as an intensive yellow powder. Melting point: decomposition with color changes from yellow to orange-red and finally to brown between 105 and 270 °C. Anal. Calcd for $ZrLi_2S_6N_4C_{54}H_{74}$: C, 60.2; H, 6.9; N, 5.2%. Found: C, 59.2; H, 6.9; N, 5.1%. ^1H NMR ($CDCl_3$, 21 °C, 200 MHz, δ in ppm): δ 1.92 (s, 24H, NCH_3), 2.12 (s, 8H, NCH_2), 2.29 (s, 18H, $C_6H_4CH_3$), 6.79 (d, 12H, C_6H_4 ortho position of CH_3, $J^{2,2} = 7.7$ Hz), 7.20 (d, 12H, C_6H_4 ortho position of thiol group, $J^{2,2} = 8.6$ Hz). ^{13}C NMR ($CDCl_3$, 21 °C, 400 MHz, δ in ppm): δ 21.1 ($C_6H_4CH_3$), 45.7 (NCH_3), 56.6 (NCH_2), 127.5 (C_6H_4), 132.4 (C_6H_4), 133.5 (C_6H_4), 140.7 (C_6H_4).

Samples of $[Li(tmeda)]_2[Zr(SC_6H_4\text{-}4\text{-}CH_3)_6]$ were dissolved in diethyl ether, which afforded large yellow single crystals after 2 weeks at −20 °C.

$[Li(tmeda)]_2[Zr(SC_6H_4\text{-}4\text{-}OCH_3)_6]$ and $[Li(THF)_3]_2[Zr(SC_6H_4\text{-}4\text{-}OCH_3)_6]$. A pale-yellow solution of $HSC_6H_4\text{-}4\text{-}OCH_3$ (1.225 g, 8.74 mmol) in diethyl ether (7 mL) was added dropwise to a slurry of $[Li(tmeda)]_2[Zr(CH_3)_6]$ (0.6 g, 1.4 mmol) at −78 °C. Immediately, gas evolution occurred and a thick yellow-orange precipitate developed. The yellow slurry was stirred for 90 min at −78 °C and then for 2 h at 21 °C. The reaction mixture was stored overnight at −15 °C. The liquid was drained, and volatiles were removed in vacuo to yield $[Li(tmeda)]_2[Zr(SC_6H_4\text{-}4\text{-}OCH_3)_6]$ (1.2 g, 1.1 mol, 79% based on $[Li(tmeda)]_2[Zr(CH_3)_6]$) as an intensive yellow powder. Melting point: decomposition with color changes from yellow to orange-red and finally to brown between 105 and 270 °C. Anal. Calcd for $ZrLi_2S_6N_4O_6C_{54}H_{74}$: C, 55.42; H, 6.37; N, 4.79%. Found: C, 52.59; H, 6.26; N, 4.79%. ^1H NMR (CD_3CN, 21 °C, 400 MHz, δ in ppm): δ 2.18 (s, 24H, NCH_3), 2.39 (s, 8H, NCH_2), 3.72 (s, 18H, $C_6H_4OCH_3$), 6.59, (d, 12H, C_6H_4 ortho to OCH_3, $J^{2,2} = 6.8$ Hz), 7.20 (d, 12H, C_6H_4 ortho to thiol group, $J^{2,2} = 6.8$ Hz).^1H NMR ($CDCl_3$, 21 °C, 400 MHz, δ in ppm): δ 1.92 (s, 24H, NCH_3), 2.13 (s, 8H, NCH_2), 3.79 (s, 18H, $C_6H_4\text{-}OCH_3$), 6.57 (d, 12H, C_6H_4 ortho to OCH_3, $J^{2,2} = 6.8$ Hz), 7.17 (d, 12H, C_6H_4 ortho to thiol group, $J^{2,2} = 6.8$ Hz). ^{13}C NMR (CD_3CN, 21 °C, 400 MHz, δ in ppm): δ 46.05 (NCH_3), 55.73 (OCH_3), 55.81 (NCH_2), 113.1 (C_6H_4), 117.49 (C_6H_4), 134.98 (C_6H_4). ^{13}C NMR ($CDCl_3$, 21 °C, 400 MHz, δ in ppm): δ 45.9 (NCH_3), 55.4 (NCH_2), 55.4 (OCH_3), 112.5 (C_6H_4), 114.6 (C_6H_4), 132.7 (C_6H_4), 134.1 (C_6H_4).

Samples of $[Li(THF)_3]_2[Zr(SC_6H_4\text{-}4\text{-}OCH_3)_6]$ were dissolved in THF, affording large yellow $[Li(tmeda)]_2[Zr(SC_6H_4\text{-}4\text{-}OCH_3)_6]$ on cooling to −20 °C for 2 weeks. ^1H NMR (CD_3CN, 21 °C, 400 MHz, δ in ppm): δ 1.79 (t, 12H, CH_2−THF), 3.63 (t, 12H, O−CH_2−THF), 3.72 (9H, $C_6H_4OCH_3$), 6.62 (6H, C_6H_4 ortho position of OCH_3, $J^{2,2} = 8.72$ Hz), 7.22 (6H, C_6H_4 ortho position of thiol group, $J^{2,2} = 8.76$ Hz). ^{13}C NMR (CD_3CN, 21 °C, 400 MHz, δ in ppm): δ 26.26 (CH_2−THF), 55.99 (OCH_3), 68.29 (O−CH_2−THF), 114.49 (C_6H_4), 115.5 (C_6H_4), 132.9 (C_6H_4), 135.44 (C_6H_4)

Crystallographic Determination of $[Li(tmeda)]_2[Zr(SC_6H_4\text{-}4\text{-}CH_3)_6]$. A chunky yellow crystal of $[Li(tmeda)]_2[Zr(SC_6H_4\text{-}4\text{-}CH_3)_6]$ with approximate dimensions of 0.25 mm × 0.20 mm × 0.20 mm was mounted on a fine glass fiber with glue. Data collection was conducted on an Enraf-Nonius CAD4 diffractometer at 213(1) K with the $\omega-2\theta$ scan technique to a maximum 2θ of 52°. The cell constants and an orientation matrix for data collection were obtained from the setting angles of 25 reflections in the range $10° < \theta < 14°$. A total of 11 659 reflections were measured, and 11 179 were found to be unique. Anisotropic decay and semiempirical absorption (ψ-scans) corrections were applied to the data set, and equivalent reflections were averaged. A quantity of 8801 reflections met the condition $F_o^2 > 3.0\sigma(F_o^2)$ and were used for additional calculations. A starting model for the structure was provided by direct methods using MULTAN.[12] The two tmeda units in the molecule are disordered, and the refined model contains two positions for the ethylene bridges with equal occupancies. The final structure model contains isotropic thermal parameters for the disordered carbon atoms of the tmeda units and anisotropic thermal parameters for all other non-hydrogen atoms. Hydrogen atoms were calculated and

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Table 1. Crystal Data and Structure Refinement for $[Li(tmeda)]_2[Zr(SC_6H_4\text{-}4\text{-}CH_3)_6]$ ($[Li(tmeda)]_2\mathbf{1}$) and $[Li(THF)_3]_2[Zr(SC_6H_4\text{-}4\text{-}OCH_3)_6]$ ($[Li(THF)_3]_2\mathbf{2}$)

	$[Li(tmeda)]_2\mathbf{1}$	$[Li(THF)_3]_2\mathbf{2}$
empirical formula	$C_{54}H_{74}Li_2N_4S_6Zr$	$C_{66}H_{90}Li_2O_{12}S_6Zr$
fw	1076.70	1372.84
temp (K)	213(1)	100(1)
wavelength (Å)	0.710 73	0.710 73
cryst syst	triclinic	hexagonal
space group	*P*-1	*R*32
a (Å)	12.606(2)	16.5924(2)
b (Å)	15.233(2)	21.7663(5)
c (Å)	16.003(4)	
α (deg)	89.93(1)	
β (deg)	108.00(2)	
γ (deg)	94.42(1)	
vol ($Å^3$), *Z*	2913(2), 2	5189.6(2), 3
ρ_{calcd} (Mg/m^3)	1.23	1.318
μ (mm^{-1})	0.427	0.397
reflns collected	11 659	10 356
data/parameters	8801/600	2284/136
R_1 [a] ($F, I > 3\sigma(I)$)	0.036	
R_1 [a] ($F, I > 2\sigma(I)$)		0.0611
wR1 [b] ($F, I > 3\sigma(I)$)	0.049	
wR2 [c] (F^2, all data)		0.1689

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR1(F) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [c] $wR2(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

included in the refinement as riding atoms with $U_{is} = 1.3U_{eq}$(bonding atom). Refinement was accomplished by the full matrix least-squares technique on *F* using all observed data. Crystallographic data are summarized in Table 1, and selected distances, angles, and torsion angles are contained in Table 2.

Crystallographic Determination of $[Li(THF)_3]_2[Zr(SC_6H_4\text{-}4\text{-}OCH_3)_6]$. A columnar yellow crystal of $[Li(THF)_3]_2[Zr(SC_6H_4\text{-}4\text{-}OCH_3)_6]$ with approximate dimensions of 0.25 mm × 0.22 mm × 0.17 mm was mounted on a fine glass fiber with glue. Preliminary examination and data collection were carried out at 100(1) K on a Siemens SMART Platform diffractometer. Intensity data were collected using 0.3° ω-scans at three different ϕ-settings corresponding to a nominal hemisphere of data. Frame time was set to 20 s. The intensities of 10 356 reflections with $2\theta < 52°$ were corrected for absorption and decay using SADABS.[13] Equivalent reflections were averaged; all 2284 unique data were used for additional calculations. The structures were solved by direct methods (SHELXS-86).[14] All non-hydrogen atoms were refined with anisotropic thermal parameters by full matrix least-squares on F^2 using all unique data (SHELXL-93).[15] No chemically reasonable model could be found to describe the disorder in the $[Li(THF)_3]^+$ group. The hydrogen atoms bonded to the aromatic ring were calculated on idealized positions and refined with isotropic thermal parameters as riding atoms. Methyl hydrogen atoms were calculated and included in the refinement with $U_{is} = 1.5U_{eq}$(bonding atom), and no hydrogen atoms of the THF unit were included in the refinement. Crystallographic data are summarized in Table 1, and selected distances, angles, and torsion angles are contained in Table 3.

Results and Discussion

Surprisingly, the reaction chemistry of the homoleptic six-coordinate perorgano complexes has received scant attention, with most attention focused on the neutral $W(CH_3)_6$ compound. These classes of complexes are attractive precursors to thiolate complexes because they can be isolated in pure form and, most importantly, on treatment with thiols, the methane side-product is unreactive and volatile, which facilitates isolation of the product. Treating $[Li(tmeda)]_2[Zr(CH_3)_6]$ with aryl thiols, $HSC_6H_4\text{-}4\text{-}R$, in a 1:6 stoichiometry in diethyl ether affords excellent yields of $[Li(tmeda)]_2[Zr(SC_6H_4\text{-}4\text{-}R)_6]$, where R = CH_3 ($\mathbf{1}^{2-}$) or OCH_3 ($\mathbf{2}^{2-}$) and (tmeda = *N*,*N*,*N′*,*N′*-tetramethylethylenediamine).

Table 2. Selected Distances (Å), Angles (deg), and Torsion Angles (deg) about Zirconium, Sulfur, and Lithium for $[Li(tmeda)]_2[Zr(SC_6H_4\text{-}4\text{-}CH_3)_6]$

Distance

Zr(1)−S(1)	2.5484(7)	S(2)−Li(1)	2.612(5)
Zr(1)−S(2)	2.5731(6)	S(3)−C(15)	1.778(2)
Zr(1)−S(3)	2.5804(5)	S(3)−Li(2)	2.569(4)
Zr(1)−S(4)	2.5767(6)	S(4)−C(22)	1.774(3)
Zr(1)−S(5)	2.5888(7)	S(4)−Li(1)	2.529(4)
Zr(1)−S(6)	2.5552(6)	S(5)−C(29)	1.774(2)
S(1)−C(1)	1.774(3)	S(5)−Li(2)	2.488(4)
S(1)−Li(2)	2.809(4)	S(6)−C(36)	1.767(2)
S(2)−C(8)	1.783(3)	S(6)−Li(1)	2.643(5)

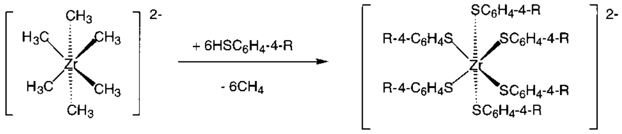
Angle

S(1)−Zr(1)−S(2)	130.47(2)	C(22)−S(4)−Li(1)	127.1(1)
S(1)−Zr(1)−S(3)	79.85(2)	Zr(1)−S(5)−C(29)	111.75(8)
S(1)−Zr(1)−S(4)	141.88(2)	Zr(1)−S(5)−Li(2)	87.2(1)
S(1)−Zr(1)−S(5)	80.57(2)	C(29)−S(5)−Li(2)	127.7(1)
S(1)−Zr(1)−S(6)	85.34(2)	Zr(1)−S(6)−C(36)	115.54(8)
S(2)−Zr(1)−S(3)	143.25(2)	Zr(1)−S(6)−Li(1)	84.89(9)
S(2)−Zr(1)−S(4)	80.18(2)	C(36)−S(6)−Li(1)	128.7(1)
S(2)−Zr(1)−S(5)	84.59(2)	S(2)−Li(1)−S(4)	80.3(1)
S(2)−Zr(1)−S(6)	79.43(2)	S(2)−Li(1)−S(6)	77.2(1)
S(3)−Zr(1)−S(4)	84.40(2)	S(2)−Li(1)−N(1)	102.0(2)
S(3)−Zr(1)−S(5)	80.58(2)	S(2)−Li(1)−N(2)	156.5(2)
S(3)−Zr(1)−S(6)	129.60(2)	S(4)−Li(1)−S(6)	77.6(1)
S(4)−Zr(1)−S(5)	130.67(2)	S(4)−Li(1)−N(1)	112.2(2)
S(4)−Zr(1)−S(6)	78.41(2)	S(4)−Li(1)−N(2)	118.9(2)
S(5)−Zr(1)−S(6)	143.63(2)	S(6)−Li(1)−N(1)	169.9(2)
Zr(1)−S(1)−C(1)	110.23(8)	S(6)−Li(1)−N(2)	93.0(2)
Zr(1)−S(1)−Li(2)	81.48(9)	N(1)−Li(1)−N(2)	83.9(2)
C(1)−S(1)−Li(2)	128.4(1)	S(1)−Li(2)−S(3)	75.3(1)
Zr(1)−S(2)−C(8)	110.99(7)	S(1)−Li(2)−S(5)	77.4(1)
Zr(1)−S(2)−Li(1)	85.2(1)	S(1)−Li(2)−N(3)	91.8(2)
C(8)−S(2)−Li(1)	122.3(1)	S(1)−Li(2)−N(4)	173.6(2)
Zr(1)−S(3)−C(15)	110.14(7)	S(3)−Li(2)−S(5)	82.7(1)
Zr(1)−S(3)−Li(2)	85.71(8)	S(3)−Li(2)−N(3)	149.8(3)
C(15)−S(3)−Li(2)	119.2(1)	S(3)−Li(2)−N(4)	105.2(2)
Zr(1)−S(4)−C(22)	113.01(8)	S(5)−Li(2)−N(3)	121.6(2)
Zr(1)−S(4)−Li(1)	86.8(1)	S(5)−Li(2)−N(4)	109.0(2)
N(3)−Li(2)−N(4)	84.7(2)		

Torsion Angle[a]

S(1)−*CS*(1)−*CS*(2)−S(2)	−110.73(3)	S(1)−*CS*(1)−*CS*(2)−S(6)	9.21(3)
S(3)−*CS*(1)−*CS*(2)−S(6)	−109.97(3)	S(5)−*CS*(1)−*CS*(2)−S(4)	−111.75(3)
S(1)−*CS*(1)−*CS*(2)−S(4)	128.15(3)	S(3)−*CS*(1)−*CS*(2)−S(2)	130.08(3)
S(5)−*CS*(1)−*CS*(2)−S(2)	9.37(3)	S(5)−*CS*(1)−*CS*(2)−S(6)	129.31(3)
S(3)−*CS*(1)−*CS*(2)−S(4)	8.96(3)		

[a] *CS*(1): center of S(1),S(3),S(5). *CS*(2): center of S(2),S(4),S(6).



Each complex is an air-sensitive canary-yellow solid soluble in hexane, diethyl ether, THF, and acetonitrile. Yellow single crystals of $[Li(tmeda)]_2\mathbf{1}$ (diethyl ether solution) or $[Li(THF)_3]_2\mathbf{2}$ (THF solution) are obtained from saturated solutions to −20 °C. Figures 1 and 2 show the X-ray structures of $[Li(tmeda)]_2\mathbf{1}$ and $[Li(THF)_3]_2\mathbf{2}$, respectively. In both complexes the zirconium atoms are solely coordinated by sulfur atoms of six aryl thiolate ligands. Bond angles about zirconium differ substantially for

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(13) Sheldrick, G. M. *SADABS*; University of Göttingen: Göttingen, Germany, 1996.
(14) Sheldrick, G. M. SHELXS-86. *Acta Crystallogr.* **1990**, *A46*, 467.
(15) Sheldrick, G. M. *SHELXL-93*; University of Göttingen: Göttingen, Germany, 1993.

Table 3. Selected Distances (Å), Angles (deg), and Torsion Angles (deg) about Zirconium, Sulfur, and Lithium for $[Li(THF)_3]_2[Zr(SC_6H_4\text{-}4\text{-}OCH_3)_6]^a$

Distance	
Zr(1)−S(1)	2.5773(12) (6×)
S(1)−C(1)	1.772(5) (6×)
S(1)−Li(1)	2.86(2) (6×)
Angle	
Zr(1)−S(1)−Li(1)	88.5(4) (6×)
S(1) −Zr(1)−S(1A)	81.32(4) (3×)
S(1) −Zr(1)−S(1B)	81.32(4) (3×)
S(1)−Zr(1)−S(1C)	86.89(5) (3×)
S(1)−Zr(1)−S(1D)	115.48(6) (3×)
S(1)−Zr(1)−S(1E)	157.83(5) (3×)
S(1)−Li(1)−S(1B)	71.9(7) (3×)
C(1)−S(1)−Zr(1)	116.4(2) (6×)
C(1)−S(1)−Li(1)	119.1(3) (6×)
O(2) −Li(1)−O(2A)	94.1(10) (3×)
O(2)−Li(1)−S(1)	90.2(3) (3×)
O(2)−Li(1)−S(1A)	102.9(3) (3×)
O(2)−Li(1)−S(1B)	162.1(9) (3×)
Torsion Angle	
S(1)−*CS*(1)−*CS*(2)−S(1C)	30.38(7) (3×)
S(1)−*CS*(1)−*CS*(2)−S(1D)	−89.62(7) (3×)
S(1)−*CS*(1)−*CS*(2)−S(1E)	150.38(7) (3×)

[a] Symmetry transformations. A: $-x + y + 1, -x + 2, z$. B: $-y + 2, x - y + 1, z$. C: $y, x, -z + 2$. D: $x - y + 1, -y + 2, -z + 2$. E: $-x + 2, -x + y + 1, -z + 2$. *CS*(1): center of S(1),S(1B),S(1A). *CS*(2): center of S(1C),S(1D),S(1E).

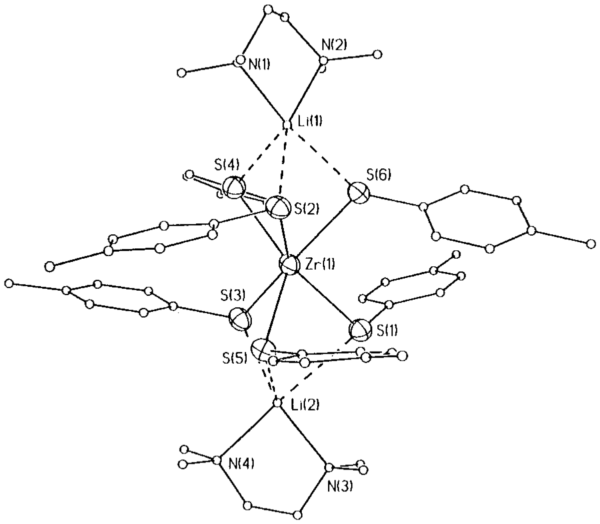

Figure 1. ORTEP plot and numbering scheme of $[Li(tmeda)]_2[Zr(SC_6H_4\text{-}4\text{-}CH_3)_6]$ with 50% probability ellipsoids for Zr and S. Other atoms are shown as spheres for clarity.

complexes $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$. The average twist angle[16] of ca. 9.18° in complex $\mathbf{1}^{2-}$ is small (trigonal prism, 0°; octahedron, 60°), and the ZrS_6 core is remarkably similar to the ZrC_6 core found[5] in $[Zr(CH_3)_6]^{2-}$. On the other hand, the twist angle of ca. 30.38° in complex $\mathbf{2}^{2-}$ is close to the midpoint of the trigonal prismatic-to-octahedral reaction coordinate and is similar to that[3g] of $[Zr(S_2C_6H_4)_3]^{2-}$. Zirconium−sulfur distances are 2.5484(7)−2.5888(7) Å (av, 2.570(14) Å) in $\mathbf{1}^{2-}$ and 2.5773(12) Å in $\mathbf{2}^{2-}$, slightly longer than in $[(CH_3)_4N]_2[Zr(S_2C_6H_4)_3]$ (2.537(2), 2.538(2), 2.555(2) Å),[3g] and fall within the range observed in $[Li(THF)]_2[Zr\{SC(CH_3)_3\}_6]$ (2.545(3), 2.638(3) Å).[17] The longer Zr−S lengths are probably due to the Li−S contacts and may represent a weakening of the Zr−S bond. The lithium cations coordinate the sulfur atoms of the triangular faces of the S_6 pseudotrigonal prism. As a result, the sulfur atoms are trigonal pyramidal with interactions with lithium, zirconium, and carbon (Figure 3). The carbon atoms are slightly out of the plane of the S_3 triangular faces inclined toward the zirconium atoms, and the C−S−*CS* (where *CS* denotes the center of the triangular face) angles are ca. 130°. The sulfur lone pairs of electrons are most likely orientated slightly out of the plane defined by the S_3 triangular face and tilted away from the zirconium atoms. A noteworthy consequence is the positioning of the lone pairs of electrons away from orthogonality with the zirconium−sulfur vector, and hence, they are poorly arranged to π-interact with zirconium.

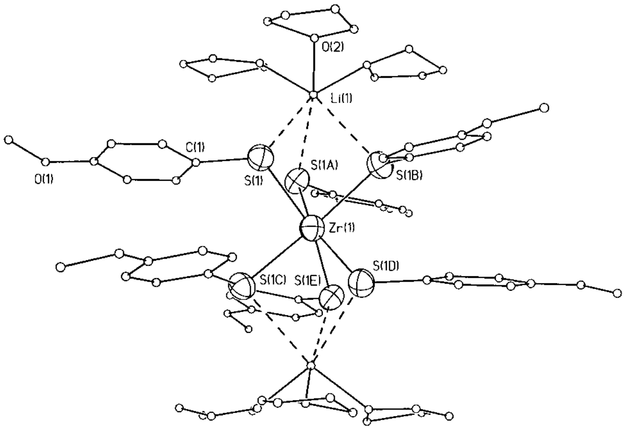

Figure 2. ORTEP plot and numbering scheme of $[Li(THF)_3]_2[Zr(SC_6H_4\text{-}4\text{-}OCH_3)_6]$ with 50% probability ellipsoids for Zr and S. Other atoms are shown as spheres for clarity.

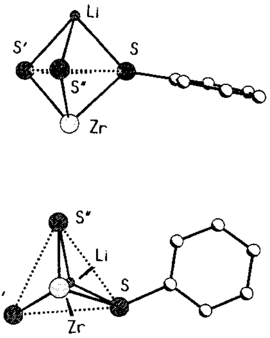

Figure 3. View of a $ZrS_2(SC_6)Li$ fragment of $[Li(THF)_3]_2[Zr(SC_6H_4\text{-}4\text{-}OCH_3)_6]$: (top) S_3 triangle perpendicular to the plane of the paper; (bottom) S_3 triangle in the plane of the paper.

Direct comparison to other complexes is difficult because homoleptic unidentate six-coordinate thiolate complexes of transition metals are very rare. Only recently, the synthesis and structure of the first mononuclear Zr(IV) thiolate containing a six-coordinated metal center, $[Li(THF)]_2[Zr\{SC(CH_3)_3\}_6]$, have been reported.[17] Unfortunately, though a nearly trigonal prismatic assignment for the central ZrS_6 core seems more likely, the possibility of an octahedral coordination geometry could not be completely dismissed because of disorder of the sulfur atoms. Close analogues of $[Li(tmeda)]_2\mathbf{1}$ and $[Li(THF)_3]_2\mathbf{2}$ are $[Na(THF)_3][Nb(SC_6H_4\text{-}4\text{-}CH_3)_6]$ and $[Na(15\text{-}crown\text{-}5)][Ta(SC_6H_5)_6]$, which were prepared[18] by treating MCl_5 (M = Nb or Ta) with $NaSC_6H_5$ or $NaSC_6H_4\text{-}4\text{-}CH_3$. Interestingly,

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(16) (a) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748−1756. (b) Dymock, K. R.; Palenik, G. J. *Inorg. Chem.* **1975**, *14*, 1220−1222.

(17) Kawaguchi, H.; Tatsumi, K.; Cramer, R. E. *Inorg. Chem.* **1996**, *35*, 4391−4395.

(18) Koo, S.-M.; Bergero, R.; Salifoglou, A.; Coucouvanis, D. *Inorg. Chem.* **1990**, *29*, 4844−4846.

$[Na(THF)_3][Nb(SC_6H_4\text{-}4\text{-}CH_3)_6]$ structurally resembles $[Li(tmeda)]_2$**1**, both containing rare, nearly trigonal prismatic MS_6 cores with alkali metal cations contacts to three sulfur atoms, while $[Na(15\text{-crown-}5)][Ta(SC_6H_5)_6]$ contains an octahedral MS_6 center with no sulfur−cation interactions.

These observations suggest that the lithium cation contact to the sulfur atoms influences the observed structures and may enhance the trigonal prismatic geometry in $[Na(THF)_3][Nb(SC_6H_4\text{-}4\text{-}CH_3)_6]$, $[Li(tmeda)]_2$**1**, and $[Li(THF)_3]_2$**2**. Support is obtained[11] with $[Ti_3(SCH_3)_{12}]$, where the central TiS_6 core is almost trigonal prismatic ($\theta = 10.69°$), and both S_3 triangular faces are capped by a $Ti(SCH_3)_3$ fragment. For the terminal TiS_6 cores in $[Ti_3(SCH_3)_{12}]$ only one triangular face is capped, causing twist angles of 49.22 and 44.50°. A similar coordination geometry is observed in $[Ti_2(SCH_3)_9]^-$ ($\theta = 31.10, 33.30°$) with one triangular face capped by a $Ti(SCH_3)_3$ fragment. Also, the $Zr(SC_6H_5)_6$ fragment in $[Zr_2(SC_6H_5)_7(CH_2C_6H_5)_2]^-$ exhibits close to trigonal prismatic coordination geometry ($\theta = 14.5°$) with one S_3 face being capped by a $Zr(SC_6H_5)(CH_2C_6H_5)_2$ moiety.[19] Additional evidence can be found in the preliminary solutions of the solid-state structure of $[Li(tmeda)]_2[Zr(SC_6H_5)_6]$ ($\theta \approx 12°$) and $[Li(tmeda)]_2[Zr(SC_6H_4\text{-}2\text{-}CH_3)_6]$ ($\theta \approx 15°$).[20] Nevertheless, the almost trigonal prismatic MC_6 center in $[Li(tmeda)]_2[Zr(CH_3)_6]$ was suggested to be intrinsic to the $Zr(CH_3)_6$ core—independent of lithium cation contacts—and caused by the electronic effect of a second-order Jahn−Teller effect[5] as described in several theoretical papers.[6,21] These studies have shown that lowering the symmetry of the ML_6 core from O_h to D_{3h} or C_{3v} is expected for six-coordinate d^0 complexes if metal−ligand interactions are primarily through σ-bonding. Furthermore, increasing the ligand's π-donor ability favors a movement from D_{3h} or C_{3v} to O_h. In contrast to organo ligands, the thiolato ligand is intrinsically a weak π-donor.[22] Contact of the ligating atoms of a weak π-donor with Lewis acids can have the effect of diminishing the ligand's π-donor ability by depleting the electron density about sulfur or by orienting the sulfur sp^3 lone pair of electrons away from the metal center. This might be the reason for the nonoctahedral structures observed for $\mathbf{1}^{2-}$, $\mathbf{2}^{2-}$, and the examples described above. In line with this suggestion is the octahedral metal core in $[Ta(SC_6H_5)_6]^-$, which is well separated from the cation.[18] Here, the thiolate ligand is unconstrained and free to optimize π-interactions. Primarily then, alkali metal cations modulate the π-donor abilities of the arylthiolato ligand in $\mathbf{1}^{2-}$, $\mathbf{2}^{2-}$, and $[Nb(SC_6H_5)_6]^-$. These results illustrate that weak secondary interactions with atoms within the metal coordination sphere might exert a strong influence on coordination geometry.

A principal difference between $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ is the replacement of a CH_3 fragment in the 4-position with a OCH_3 group, leading to stronger electron donation to the ligating sulfur atom through resonance effects. Consequently, the thiolato ligand in $\mathbf{2}^{2-}$ possesses enhanced electron richness at sulfur. Increased trigonal twist away from the trigonal prismatic limit toward the octahedral is expected regardless of whether the root cause is increased π-interaction or electrostatic repulsion. A twist from trigonal prismatic caused by increased π-interactions should be reflected in a shortening of the Zr−S bond distances. This is not observed in a comparison of bond lengths in $\mathbf{1}^{2-}$ (av, 2.570(14) Å) and $\mathbf{2}^{2-}$ (2.5773(12) Å). Conceivably, electrostatics may play a role in determining the MS_6 geometry in $\mathbf{2}^{2-}$, which raises the important point that electrostatic and electronic contributions are at work.

In summary, this work extends the application of computational studies from hexaorgano to hexathiolato d^0 metal complexes. The intrinsically weak π-donor thiolate ligand is possibly converted to a primarily σ-bonding system by interaction of one of its lone pairs of electrons with a Lewis acid, as indicated by the trigonal prismatic MS_6 geometry in $\mathbf{1}^{2-}$. In $\mathbf{2}^{2-}$ the movement away from the expected trigonal prismatic geometry could be due to either π-interactions or electrostatic repulsion. The ability to modify the aryl group allows these factors to be further investigated. We are examining correlations of twist angles with Hammett σ_I parameters, thiol pK_a values, and ionic potentials of the cation.

As a final remark, owing to the scarcity of data available at this time, simple crystal packing effects cannot be entirely excluded.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of $[Li(tmeda)]_2$**1** and $[Li(THF)_3]_2$**2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Reference 5 and references therein.
(22) Ashby, M. T. *Comments Inorg. Chem.* **1990**, *10*, 297−313.