and R_w = 3.73% for 336 parameters refined against those 2557 reflections with $|F_o| > 6\sigma|F_o|$ and R = 8.35% for all data. Final atomic coordinates appear in Table IV.

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Supplementary Material Available: Tables of anisotropic thermal parameters and calculated positions for hydrogen atoms (3 pages). Ordering information is given on any current masthead page.

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C–S Bond Cleavage at an Electrophilic Zirconium Center: Synthesis, Structure, and Thermal Decomposition of $[Cp_2Zr(S\text{-}t\text{-}C_4H_9)(THF)][BPh_4]$

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Summary: Protonolysis of $[Cp_2ZrCH_3(THF)][BPh_4]$ with *tert*-butyl mercaptan leads to the (thiolato)zirconocene cation $[Cp_2Zr(S\text{-}t\text{-}C_4H_9)(THF)][BPh_4]$ in 79% yield. In addition to the usual spectroscopic methods the complex was characterized by X-ray crystallography (monoclinic, $P2_1/c$, a = 10.111 (4) Å, b = 18.6066 (18) Å, c = 19.408 (7) Å, β = 94.31 (2)°, Z = 4, R = 0.036). Structural parameters and THF exchange rates point to a less electrophilic Zr center than in the parent alkyl species. Nevertheless, the center is electrophilic enough to induce C–S bond cleavage under thermal duress.

Introduction

Much attention has recently been directed toward d^0 group 4 metallocene alkyl cations of general formula $[Cp_2M(R)(B)][BAr_4]$, where Cp is a cyclopentadienyl donor, B is some stabilizing Lewis base, and the counterion is a noncoordinating tetraarylborate anion.[1] With the exception of alkoxides,[2] uninegative heteroatom-containing donors isoelectronic with hydrocarbyl ligands have not been used in place of R in $[Cp_2M(R)(B)][BAr_4]$. We are seeking convenient routes for incorporation of higher chalcogenato ligands ($^-$SR, $^-$SeR, $^-$TeR) into these cations to explore the reactivity of the resultant hard metal–soft element bonds. Herein we report our initial results on the synthesis and thermal decomposition of a *tert*-butyl mercaptan–zirconocene cation, 1a, which occurs by heterolytic cleavage of the alkanethiolato C–S bond, an important primary step in hydrosulfurization procedures.[3]

Experimental Section

General Considerations. All operations were performed under a purified argon atmosphere in a Braum MB-150 inert-atmosphere glovebox or on high-vacuum lines using standard techniques.[4] Solvents were purified as follows: toluene was distilled from sodium benzophenone ketyl and stored over "titanocene";[5] tetrahydrofuran (THF) was predried with activated (10^{-4} Torr, 200 °C, 3 h) 3-Å molecular sieves, distilled from and stored over sodium benzophenone ketyl; hexanes were distilled from lithium aluminum hydride (Aldrich) and stored over "titanocene"; dichloromethane was distilled from CaH_2; benzene-d_6 was dried sequentially over activated 3-Å sieves and "titanocene" and stored in the glovebox; other NMR solvents were dried analogously to the perprotio solvents. Unless otherwise mentioned, reagents were obtained from commercial suppliers and used as received. $Cp_2Zr(CH_3)_2$[6] was made by a published method and reacted with 2,6-di-*tert*-butylpyridinium tetraphenylborate (1:1 in THF) to obtain $[Cp_2Zr(CH_3)(THF)][BPh_4]$. Thiols (*stench!*) were dried, degassed, and stored over activated 3-Å molecular sieves and used only on the vacuum line or in a well-ventilated fume hood.

^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on a Varian Gemini 200 or Unity 400 instrument using Wilmad 528-PP NMR tubes. Variable-temperature NMR experiments were performed on samples sealed in 5-mm NMR tubes under ≈700 mm of argon purified by passing through activated 3-Å molecular seives and MnO on vermiculite. Microanalyses were performed by Onieda Research Services, Inc., One Halsey Rd., Whitesboro, NY 13492.

Synthesis of 2,6-Di-*tert*-butylpyridinium Tetraphenylborate. To a solution of 2,6-di-*tert*-butylpyridine (6.6 mL, 29.2 mmol) in 25 mL of methanol under nitrogen atmosphere was added 2.4 mL (29.2 mmol) of concentrated HCl. The solution was stirred for 15 min and diluted with 100 mL of deionized water. Solid $NaBPh_4$ (10.0 g, 29.2 mmol) was added in portions and the resulting slurry stirred for 2 h. The white product was isolated by filtration and washed twice with 50-mL portions of deionized water and dried in vacuo for 24 h. Yield: 13.4 g, 90%. ^1H NMR (200 MHz, CD_3CN, ppm): C–H_p, 8.34 (t, J = 8.4 Hz, 1 H); C–H_m, 7.82 (d, 2 H); $B(C_6H_5)_4$, 7.28 (m, 8 H, ortho), 6.99 (m, 8 H, meta), 6.83 (m, 4 H, para); $C(CH_3)_3$, 1.51 (s, 18 H); N–H, not observed.

Synthesis of $[Cp_2Zr(S\text{-}t\text{-}C_4H_9)(THF)][BPh_4]$ (1a). $[Cp_2Zr(CH_3)(THF)][BPh_4]$ (1.045 g, 1.69 mmol) was loaded into a 50-mL round-bottomed flask and attached to a swivel frit assembly equipped with a 90° needle valve adaptor. A 30-mL volume of dry dichloromethane was vacuum transferred into the vessel, and after dissolution of the methyl cation, the pale yellow solution was cooled to −78 °C. *tert*-Butyl mercaptan (0.19 mL, 1.69 mmol) was introduced via vacuum transfer from a graduated

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tube attached to the vacuum line through a 180° needle valve. The reaction was placed under an atmosphere of argon and allowed to warm to room temperature while open to a mercury bubbler. A slow deepening of the yellow color of the solution was accompanied by the evolution of gas bubbles. When gas production had visibly stopped, the reaction was stirred a further 15 min and the solvent removed in vacuo. THF (≈20 mL) was vacuum transferred into the vessel and the resulting suspension filtered to yield 0.926 g (79%) of bright yellow microcrystals of **1a**. ^{1}H NMR (200 MHz, CD_2Cl_2, ppm): $B(C_6\mathit{H}_5)_4$, 7.36 (br m, 8 H, ortho), 7.07 (t, J = 7.2 Hz, 8 H, meta) 6.91 (t, J = 7.2 Hz, 4 H, para); $C_5\mathit{H}_5$, 6.37 (s, 10 H); $O(C\mathit{H}_2CH_2)_2$, 3.57 (m, 4 H); $O(CH_2C\mathit{H}_2)_2$, 1.83 (m, 4 H); $SC(C\mathit{H}_3)_3$, 1.59 (s, 9 H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, ppm): $B(\mathit{C}_6H_5)_4$, 163.1 (ipso, q, J_{BC} = 48 Hz), 136.4 (meta); 126.1 (q, J_{BC} = 2.6 Hz, ortho); 122.2 (para); C_5H_5, 114.6; $O(\mathit{C}H_2CH_2)_2$, 80.99; $SC(\mathit{C}H_3)_3$, 35.86; $O(CH_2\mathit{C}H_2)_2$, 26.25; $S\mathit{C}(CH_3)_3$, obscured by solvent. Anal. Calcd for $C_{42}H_{47}BOSZr$: C, 71.87; H, 6.75. Found: C, 71.71; H, 6.53.

Synthesis of [Cp$_2$Zr(S-*t*-C$_4$H$_9$)(DMAP)][BPh$_4$] (1b). [Cp$_2$Zr(THF)(S-*t*-Bu)][BPh$_4$] (0.781 g, 1.11 mmol) and DMAP (0.1305, 1.07 mmol) were combined in a 50-mL round-bottomed flask and attached to a swivel frit assembly. THF (20 mL) was vacuum transferred into the vessel, and the reaction mixture was stirred at room temperature until the green to pale orange color change was complete (2 h), at which time solvent was removed in vacuo. The remaining solid was recrystallized from THF–toluene (1:2) yielding a crop of pale orange crystals (0.787 g, 94%) after washing with cold toluene. ^{1}H NMR (200 MHz, CD_2Cl_2, ppm): $N(C\mathit{H}CH)_2CN(CH_3)_2$, 7.62 (s, 2 H); $N(CHC\mathit{H})_2CN(CH_3)_2$, 7.59 (s, 2 H); $B(C_6\mathit{H}_5)_4$, 6.94 (br m, 8 H, ortho); 6.70 (m, 8 H, meta); 6.58 (t, J = 6.1 Hz, 4 H, para); $C_5\mathit{H}_5$, 6.35 (s, 10 H); $N(C\mathit{H}_3)_2$, 3.01 (s, 6 H); $SC(C\mathit{H}_3)_3$, 1.61 (s, 9 H). ^{13}C{^{1}H} NMR (50 MHz, CD_2Cl_2, ppm): $B(\mathit{C}_6H_5)_4$, 162.5 (ipso, q, J_{BC} = 49 Hz); $N(\mathit{C}HCH)_2CN(CH_3)_2$, 150.0; $B(\mathit{C}_6H_5)_4$, 136.3 (meta); 126.0 (q, J_{BC} = 2.7 Hz, ortho); 122.1 (para); C_5H_5, 114.3; $N(CH\mathit{C}H)_2CN(CH_3)_2$, 107.9; $N(\mathit{C}H_3)_2$, 39.8; $SC(\mathit{C}H_3)_3$, 35.9; $S\mathit{C}(CH_3)_3$, obscured by solvent. Anal. Calcd for $C_{45}H_{49}BN_2SZr$: C, 71.87; H, 6.57; N, 3.73. Found: C, 71.12; H, 6.14; N, 3.54.

Measurement of THF Exchange Rates in 1a. Approximate rates of exchange between free and coordinated THF in CD_2Cl_2 solutions (two concentrations) of **1a** and THF were determined by variable-temperature ^{1}H NMR experiments. Samples were prepared by loading freshly recrystallized **1a** (6.0 mg, 8.6×10^{-3} mmol, [**1a**] = 0.012 M; 11.0 mg, 1.56×10^{-2} mmol, [**1a**] = 0.022 M) into a sealable 5-mm NMR tube and adding 0.7 mL of CD_2Cl_2 at −78 °C to avoid any decomposition of **1a** to chloride-containing neutral derivatives. One equivalent of THF was admitted by vacuum transferring the appropriate pressure from an 11.4-mL constant-volume bulb; integration of free vs coordinated THF resonances indicated that [Zr]:[THF] = 1:1 ± 0.1. Exchange rates were evaluated at the coalescence temperature of 213 ± 4 K for the β protons of free and coordinated THF using the equation $k = \pi\delta_{AB}/\sqrt{2}$,[7] where δ_{AB} is approximated as the ultimate peak separation at the low-temperature limit ($[Zr]_1$ = 0.012 M, k_2 = 97 s^{-1}; $[Zr]_2$ = 0.022 M, k_2 = 143 s^{-1}).

Thermal Decomposition of 1a. A solution of **1a** (11.2 mg in 0.07 mL of THF-d_8, 0.023 M) was loaded into a sealable 5-mm NMR tube and flame sealed under ≈700 mmHg. The sample was placed into an oil bath heated to 97 °C and the decomposition monitored periodically by room-temperature ^{1}H NMR. The concentration of **1a** was evaluated by the relative integrals of the cyclopentadienyl resonances of **1a** and $[Cp_2ZrS]_2$ (6.48 and 6.44 ppm, respectively). Spectra were accumulated with a 45° pulse and a 20-s relaxation delay to ensure reliable integrations were obtained.

X-ray Crystal Structure of [Cp$_2$Zr(S-*t*-C$_4$H$_9$)(THF)][BPh$_4$] (1a). Single crystals of **1a** were grown from a saturated THF solution in a flame-sealed tube at room temperature. A crystal suitable for X-ray crystallography was mounted and sealed in a quartz capillary and optically centered in the X-ray beam of an Enraf-Nonius CAD-4 diffractometer. Details of crystal data, data collection, and structure refinement parameters are presented in Table I. Structure solution proceeded routinely following location of the Zr and S atoms through direct methods. After anisotropic refinement of all non-hydrogen atoms C_5 and C_6 ring hydrogen atoms were fixed in calculated positions (d_{C-H} = 1.08 Å) with temperature factors based upon the carbon atom to which they are bonded. Methyl hydrogen atoms were located via inspection of a difference Fourier map and fixed to the appropriate carbon atom. Final fractional coordinates and equivalent isotropic thermal parameters are give in in Table II. All crystallographic calculations were conducted with the PC version of the NRCVAX program package locally implemented on an IBM compatibile 80486 computer.

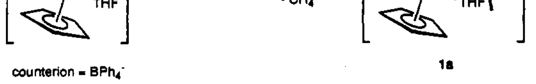
Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

compd	$[Cp_2Zr(C_4H_9S)(THF))]BPh_4$
color	pale yellow
fw	701.9
cryst system	monoclinic
space group	$P2_1/c$
temp, °C	17
cell constants[a]	
a, Å	10.111 (4)
b, Å	18.6066 (18)
c, Å	19.408 (7)
β, deg	94.310 (20)
cell vol, Å^3	3640.9 (20)
$F(000)$	1472
Z	4
D_{calc}, g cm^{-3}	1.281
μ_{calc}, cm^{-1}	3.8
scan type	$\omega/2\theta$
radiation	Mo Kα
max xtal dimens, mm	0.30 × 0.40 × 0.60
scan width	0.70 + 0.35 tan θ
transm range	0.844, 0.999
decay of stds	±1%
no. of reflcns measd	5715
2θ range, deg	2–47
no. of unique reflcns	5372
no. of reflcns obsd[b]	4232
computer programs[c]	NRCVAX[d]
structure solution	direct
no. of params	415
weight modifier, k	0.00002
GOF	3.36
R	0.036
R_w	0.040
final diff map, e/Å^3	0.36

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ for 25 reflections $\theta >$ 15°. [b] $I > 3.0\sigma(I)$. Corrections: Lorentz-polarization and absorption (empirical ψ scan). [c] Neutral scattering factors and anomalous dispersion corrections from reference. [d] An Interactive Program System for Structure Analysis written by E. J. Gabe, Y. Le Page, J.-P. Charland, F. L. Lee, and P. S. White: *J. Appl. Crystallogr.* **1989**, *22*, 384.

Results and Discussion

A cationic (thiolato)zirconocene derivative was accessed by a protonolysis route which involved treatment of the well-known THF-stabilized methyl cation [Cp$_2$Zr(CH$_3$)(THF)][BPh$_4$][1] with 1 equiv of *t*-BuSH in dichloromethane (eq 1). Steady gas evolution over the course of ≈30 min (presumably methane) accompanied a deepening of the solution's yellow color. The product [Cp$_2$Zr(S-*t*-Bu)(THF)][BPh$_4$] (**1a**) was isolated as a yellow precipitate in excellent yield (79%) after substitution of CH_2Cl_2 for pure THF. Like many cationic group 4 metallocene derivatives, **1a** retains one THF ligand in zirconium's coordination



1a

(1)

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Table II. Atomic Parameters *x*, *y*, *z* and B_{iso} Values[a] for $[Cp_2Zr(C_4H_9S)(THF)]BPh_4$, Where Esd's Refer to the Last Digit Printed

	x	y	z	B_{iso}, Å
Zr	0.83885 (4)	0.393641 (18)	0.217337 (17)	3.107 (15)
S	1.01115 (10)	0.43676 (5)	0.30389 (5)	4.14 (4)
O	0.67450 (24)	0.40345 (14)	0.28604 (12)	4.44 (12)
Cp(1)	0.7346 (8)	0.5047 (3)	0.16504 (24)	6.8 (3)
Cp(2)	0.8648 (9)	0.5093 (3)	0.1559 (3)	8.1 (4)
Cp(3)	0.8984 (5)	0.4556 (4)	0.1114 (3)	7.0 (3)
Cp(4)	0.7830 (7)	0.41821 (24)	0.09221 (20)	6.1 (3)
Cp(5)	0.6813 (5)	0.4477 (3)	0.12642 (25)	5.9 (3)
Cp(6)	0.9093 (5)	0.27739 (20)	0.27717 (21)	4.62 (20)
Cp(7)	0.7850 (5)	0.26422 (22)	0.2405 (3)	5.8 (3)
Cp(8)	0.8014 (5)	0.27122 (22)	0.1693 (3)	5.48 (23)
Cp(9)	0.9352 (5)	0.28758 (20)	0.16222 (21)	4.70 (21)
Cp(10)	1.0007 (4)	0.29144 (19)	0.22833 (21)	4.18 (19)
C(1)	1.0305 (5)	0.53171 (24)	0.33322 (24)	5.97 (23)
C(2)	0.9011 (6)	0.5714 (3)	0.3333 (3)	9.7 (4)
C(3)	1.0871 (9)	0.5251 (4)	0.4070 (4)	15.3 (5)
C(4)	1.1296 (7)	0.5675 (4)	0.2939 (5)	14.6 (6)
C(5)	0.6934 (5)	0.3911 (3)	0.36071 (21)	7.4 (3)
C(6)	0.5703 (6)	0.3687 (3)	0.3829 (3)	8.0 (3)
C(7)	0.4657 (4)	0.3916 (3)	0.33182 (25)	6.3 (3)
C(8)	0.5336 (5)	0.4053 (3)	0.2685 (3)	7.6 (3)
B	0.7335 (4)	0.71467 (21)	0.01426 (19)	3.02 (18)
C(11)	0.7125 (3)	0.64656 (18)	−0.03896 (17)	3.07 (15)
C(12)	0.7382 (4)	0.65398 (19)	−0.10916 (18)	3.78 (17)
C(13)	0.7359 (4)	0.59739 (24)	−0.15462 (18)	4.45 (20)
C(14)	0.7053 (4)	0.52863 (22)	−0.13272 (20)	4.54 (19)
C(15)	0.6780 (4)	0.51829 (20)	−0.06441 (20)	4.72 (21)
C(16)	0.6828 (4)	0.57649 (20)	−0.01904 (18)	3.94 (18)
C(21)	0.6588 (3)	0.78753 (18)	−0.01611 (17)	3.05 (15)
C(22)	0.6938 (4)	0.85608 (20)	0.00820 (18)	3.67 (16)
C(23)	0.6299 (4)	0.91837 (20)	−0.01647 (21)	4.49 (19)
C(24)	0.5234 (4)	0.91298 (22)	−0.06454 (22)	5.08 (21)
C(25)	0.4820 (4)	0.84657 (23)	−0.08863 (21)	4.98 (20)
C(26)	0.5500 (4)	0.78507 (20)	−0.06488 (19)	4.14 (18)
C(31)	0.6700 (3)	0.69833 (17)	0.08873 (17)	2.95 (16)
C(32)	0.7360 (4)	0.71248 (20)	0.15310 (18)	3.85 (17)
C(33)	0.6780 (4)	0.70028 (22)	0.21503 (18)	4.53 (20)
C(34)	0.5508 (4)	0.67307 (21)	0.21474 (19)	4.36 (19)
C(35)	0.4819 (4)	0.65880 (21)	0.15190 (21)	4.47 (20)
C(36)	0.5407 (4)	0.67199 (20)	0.09030 (18)	3.78 (18)
C(41)	0.8971 (3)	0.72291 (18)	0.2534 (16)	3.00 (15)
C(42)	0.9711 (4)	0.66632 (20)	0.5634 (19)	3.90 (17)
C(43)	1.1078 (4)	0.66644 (21)	0.06487 (20)	4.27 (19)
C(44)	1.1788 (4)	0.7237 (3)	0.04156 (19)	4.44 (20)
C(45)	1.1097 (4)	0.78000 (21)	0.00966 (19)	4.18 (18)
C(46)	0.9724 (4)	0.77954 (19)	0.00189 (17)	3.44 (17)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

sphere, even under high vacuum (10^{-4} mmHg). Exchange with free THF in solution occurs at an intermediate rate ($k = (7.3 \pm 0.8) \times 10^3$ M^{-1} s^{-1} at 213 K) compared to the rates observed for exchange in the methyl cation ($k = 2.81 \times 10^4$ M^{-1} s^{-1} at 188 K[8]) and the *tert*-butoxy analog, $[Cp_2Zr(O\text{-}t\text{-}C_4H_9)(THF)][BPh_4]$ (**2**) $k = 2.37 \times 10^2$ M^{-1} s^{-1} at 249 K[2d]). The THF ligand may be displaced by other, stronger donors, for example *N,N*-dimethylaminopyridine (eq 2).

$$[Cp_2Zr(S\text{-}t\text{-}C_4H_9)(THF)][BPh_4] + DMAP \xrightarrow{THF} \underset{\textbf{1b}}{[Cp_2Zr(S\text{-}t\text{-}C_4H_9)(DMAP)][BPh_4]} + THF \quad (2)$$

This particular route to thiolato cations of zirconocene does not appear to be general. For example, more acidic arenethiols (e.g. Ar = 3,5-dimethylphenyl, pK_a 5–7[9]) react to give neutral thiolato compounds (a mixture of $Cp_2Zr(SAr)_2$ and $Cp_2Zr(SAr)(CH_3)$), BPh_3, and benzene.

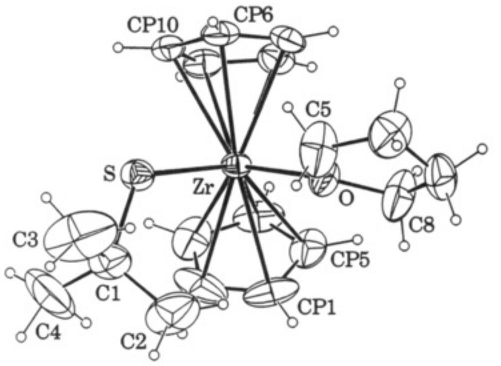

Figure 1. ORTEP diagram of **1a**. Atoms are drawn as 50% probability thermal ellipsoids.

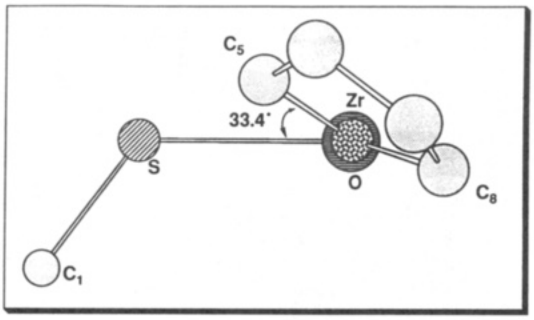

Figure 2. Chem 3D drawing of the molecular core of **1a**, looking down the Zr–O bond and illustrating the orientation of the coordinated THF ligand with respect to the plane bisecting the axis.

Analogous side reactions proceed when less bulky alkyl groups (R = $CH_2CH(CH_3)CH_2CH_3$, p$K_a \approx 10$) on sulfur are employed. A similar sensitivity to the nature of R was observed in the reactions of alcohols with $[Cp_2Zr(CH_3)(THF)][BPh_4]$,[2d] and we are currently seeking a more general route to other (thiolato)zirconocene cations.

Interestingly, **1a** is *not* isostructural (Figure 1, Table III) with the congeneric *tert*-butoxy cation **2**. The most obvious difference is the change in hybridization at E as indicate by the observed Zr–E–C angles: 169.8 (2)° (E = O); 124.80 (15)° (E = S). This trend in X–E–X bond angles is well documented[10] and is attributed to both the lower electronegativity and larger size of sulfur compared to oxygen. Another contrast between the two structures lies in the extent of π bonding between zirconium and its two reactive ligands. In **2**, the alkoxide acts as a strong π donor while the THF ligand does not appreciably participate in π bonding to Zr.[2d] While the bent orientation of the thiolato ligand in **1a** does not preclude π bonding on symmetry grounds, sulfur's larger atomic radius and the soft, diffuse nature of 3p versus the 2p orbital leads to less effective π overlap with the $1a_1$[11] orbital on the hard zirconium(IV) center. This is supported by the obserbed Zr–S distance of 2.4618 (13) Å in **1a**, which compares favorably with the range of known terminal Zr–S single bond lengths of 2.42–2.50 Å[12] indicating that little double-bond character exists in the Zr–S linkage. Interestingly, the THF ligand in **1a** does not appear to be compensating by π interacting to its maximum capability. As shown in

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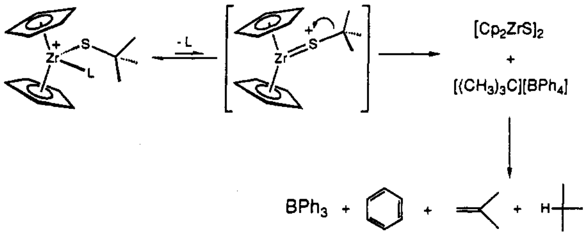
Table III. Interatomic Distances (Å) and Angles (deg) for [Cp$_2$Zr(C$_4$H$_9$S)(THF)]BPh$_4$

	Distances		
Zr–S	2.4618 (13)	C(7)–C(8)	1.475 (7)
Zr–O	2.2150 (25)	B–C(11)	1.639 (5)
Zr–Cp(1)	2.500 (4)	B–C(21)	1.639 (5)
Zr–Cp(2)	2.484 (5)	B–C(31)	1.653 (5)
Zr–Cp(3)	2.471 (4)	B–C(41)	1.660 (5)
Zr–Cp(4)	2.494 (4)	C(11)–C(12)	1.413 (5)
Zr–Cp(5)	2.498 (4)	C(11)–C(16)	1.399 (5)
Zr–Cp(6)	2.532 (4)	C(12)–C(13)	1.373 (5)
Zr–Cp(7)	2.517 (4)	C(13)–C(14)	1.390 (6)
Zr–Cp(8)	2.480 (4)	C(14)–C(15)	1.387 (6)
Zr–Cp(9)	2.479 (4)	C(15)–C(16)	1.394 (5)
Zr–Cp(10)	2.507 (4)	C(21)–C(22)	1.396 (5)
S–C(1)	1.862 (4)	C(21)–C(26)	1.397 (5)
O–C(5)	1.465 (5)	C(22)–C(23)	1.394 (5)
O–C(8)	1.440 (5)	C(23)–C(24)	1.375 (6)
Cp(1)–Cp(2)	1.344 (12)	C(24)–C(25)	1.375 (6)
Cp(1)–Cp(5)	1.384 (9)	C(25)–C(26)	1.395 (5)
Cp(2)–Cp(3)	1.380 (11)	C(31)–C(32)	1.396 (5)
Cp(3)–Cp(4)	1.385 (10)	C(31)–C(36)	1.399 (5)
Cp(4)–Cp(5)	1.379 (8)	C(32)–C(33)	1.395 (5)
Cp(6)–Cp(7)	1.418 (7)	C(33)–C(34)	1.381 (6)
Cp(6)–Cp(10)	1.398 (6)	C(34)–C(35)	1.384 (6)
Cp(7)–Cp(8)	1.411 (7)	C(35)–C(36)	1.396 (5)
Cp(8)–Cp(9)	1.404 (7)	C(41)–C(42)	1.401 (5)
Cp(9)–Cp(10)	1.401 (6)	C(41)–C(46)	1.396 (5)
C(1)–C(2)	1.503 (8)	C(42)–C(43)	1.380 (6)
C(1)–C(3)	1.506 (8)	C(43)–C(44)	1.380 (6)
C(1)–C(4)	1.465 (9)	C(44)–C(45)	1.380 (6)
C(5)–C(6)	1.410 (7)	C(45)–C(46)	1.385 (5)
C(6)–C(7)	1.458 (8)		
Zr–Cent1	2.196 (3)	Zr–Cent2	2.1978 (22)
	Angles		
S–Zr–O	94.98 (7)	C(21)–B–C(41)	113.4 (3)
Cp(2)–Cp(1)–Cp(5)	108.8 (5)	C(31)–B–C(41)	110.6 (3)
Cp(1)–Cp(2)–Cp(3)	109.0 (5)	B–C(11)–C(12)	120.5 (3)
Cp(2)–Cp(3)–Cp(4)	106.9 (5)	B–C(11)–C(16)	124.5 (3)
Cp(3)–Cp(4)–Cp(5)	108.3 (5)	C(12)–C(11)–C(16)	114.6 (3)
Cp(1)–Cp(5)–Cp(4)	106.9 (5)	C(11)–C(12)–C(13)	123.3 (3)
Cp(7)–Cp(6)–Cp(10)	107.4 (4)	C(12)–C(13)–C(14)	120.2 (3)
Cp(6)–Cp(7)–Cp(8)	108.1 (4)	C(13)–C(14)–C(15)	119.0 (3)
Cp(7)–Cp(8)–Cp(9)	107.5 (4)	C(14)–C(15)–C(16)	119.7 (4)
Cp(8)–Cp(9)–Cp(10)	108.3 (4)	C(11)–C(16)–C(15)	123.2 (3)
Cp(6)–Cp(10)–Cp(9)	108.7 (4)	B–C(21)–C(22)	122.4 (3)
S–C(1)–C(2)	113.3 (4)	B–C(21)–C(26)	122.3 (3)
S–C(1)–C(3)	103.7 (4)	C(22)–C(21)–C(26)	115.2 (3)
S–C(1)–C(4)	109.4 (4)	C(21)–C(22)–C(23)	123.0 (3)
C(2)–C(1)–C(3)	108.0 (5)	C(22)–C(23)–C(24)	119.4 (4)
C(2)–C(1)–C(4)	114.0 (5)	C(23)–C(24)–C(25)	119.9 (3)
C(3)–C(1)–C(4)	107.9 (6)	C(24)–C(25)–C(26)	119.7 (4)
O–C(5)–C(6)	107.2 (4)	C(21)–C(26)–C(25)	122.7 (4)
C(5)–C(6)–C(7)	108.5 (4)	B–C(31)–C(32)	123.8 (3)
C(6)–C(7)–C(8)	105.0 (4)	B–C(31)–C(36)	120.6 (3)
O–C(8)–C(7)	108.2 (4)	C(32)–C(31)–C(36)	115.5 (3)
C(5)–O–C(8)	106.9 (3)	C(31)–C(32)–C(33)	122.5 (3)
C(11)–B–C(21)	112.2 (3)	C(32)–C(33)–C(34)	120.5 (3)
C(11)–B–C(31)	111.6 (3)	C(33)–C(34)–C(35)	118.8 (3)
C(11)–B–C(41)	103.5 (3)	C(34)–C(35)–C(36)	120.1 (4)
C(21)–B–C(31)	105.5 (3)	C(31)–C(36)–C(35)	122.6 (3)
B–C(41)–C(42)	118.8 (3)	C(44)–C(45)–C(46)	120.9 (4)
B–C(41)–C(46)	126.2 (3)	C(41)–C(46)–C(45)	122.4 (3)
C(42)–C(41)–C(46)	114.9 (3)	Zr–S–C(1)	124.80 (15)
C(41)–C(42)–C(43)	123.2 (3)	Zr–O–C(5)	122.31 (23)
C(42)–C(43)–C(44)	120.2 (3)	Zr–O–C(8)	129.26 (24)
C(43)–C(44)–C(45)	118.3 (3)	Cent1–Zr–Cent2	127.0 (3)

Figure 2, the THF ligand is rotated 57° out of the perpendicular orientation associated with maximum π overlap to the empty Zr 1a$_1$ orbital;[13] in addition the Zr–O distance of 2.2150 (25) Å is consistent with the values observed for in-plane, non-π-bonding THF ligands (2.20–2.23 Å).[1] Since a perpendicular orientation is expected to be electronically favorable in the absence of π donation from SR, perhaps the superior σ-donating ability of -SR vs -OR allows the THF ligand to rotate closer to the sterically less demanding in-plane orientation.

The structural features discussed above point to a more electrophilic zirconium center in **1a** compared with **2**. The relative rates of exchange between bound and free THF in these complexes (vide supra) also support this notion, since THF exchange by an associative mechanism[1] would be accelerated at the more electron-deficient metal center. Thus, the observed rate is slow for **2** in which the Zr center is stabilized by substantial π bonding from OR and faster for the more electron-deficient thiolato derivative.

While attempting to grow crystals of **1a**, we discovered that it is unstable in THF toward sulfur–carbon bond cleavage at moderate temperatures (eq 3). The decomposition is very clean, producing the known sulfide-bridged dimer[14] as the exclusive zirconium-containing product. The other products (CH$_2$═C(CH$_3$)$_2$, HC(CH$_3$)$_3$, C$_6$H$_6$, B(C$_6$H$_5$)$_3$) arise from the decomposition of putative "[(CH$_3$)$_3$C]$^+$[BPh$_4$]$^-$" and were identified by ^{1}H and ^{11}B NMR spectroscopy. The decomposition is quite slow when carried out in THF-d_8 (first order in **1a**, k_r = 5.2 (5) × 10^{-4} s^{-1}, $t_{1/2} \approx$ 25 min at 97 °C, [**1a**] = 0.024 mol L^{-1}) but qualitatively much faster in CD$_2$Cl$_2$. Unfortunately, decomposition experiments carried out in chlorinated solvents (CD$_2$Cl$_2$, Cl$_2$DCCDCl$_2$) were complicated by competing chloride-transfer side reactions,[15] a hindrance which has thus far precluded accurate kinetic studies aimed at determining the THF dependence. Nonetheless, it is apparent that **1a** decomposes to [Cp$_2$ZrS]$_2$ more rapidly in CD$_2$Cl$_2$ and thus qualitatively the evidence suggests an inverse dependence of [THF] requiring that THF dissociation to form a "base-free" intermediate precedes the carbon–sulfur cleavage step. Further circumstantial support for this notion is found in the observed thermal stability of the DMAP adduct **1b**, which remains unchanged even after heating at 98 °C for 24 h in THF. In this compound, dissociation of the strongly σ-bonded DMAP ligand is unfavorable and C–S bond breakage is prevented. Last, we note that the observed ground-state C–S bond length in **1a** of 1.862 (4) Å is only slightly elongated from the calculated distance of 1.82 Å,[16] suggesting that a more electrophilic, unsolved zirconium center is required for C–S cleavage to proceed.[17]



(3)

Conclusion

Although C–S bond breakage is a relatively common decomposition pathway for *tert*-butyl mercaptan ligands,[18]

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(17) (a) Analogous thermal decomposition studies on the alkoxy congener **2** have not been reported. We have, however, observed the thermal decomposition of other alkoxy cations, and preliminary observations suggest the decomposition proceeds via C–O bond cleavage.[17b] (b) Piers, W. E. Unpublished observations.

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usually two or more metal centers are required to activate the SR ligand in this manner.[19] In the few cases where a single metal center abstracts sulfur from alkane thiols or thioethers, it is in a high oxidation state and therefore an exceedingly electrophilic center.[20] Provided a more general synthetic route to other cationic zirconocene thiolato derivatives may be uncovered, potential exists for a more detailed study of the C–S bond-cleavage step in these systems. We are also exploring the possibility of trapping the presumed intermediate, "$Cp_2Zr{=}S$", which should be highly reactive.[21]

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Supplementary Material Available: Tables of hydrogen atom parameters, crystallographic details, anisotropic thermal parameters, and complete interatomic distances and angles (7 pages). Ordering information is given on any current masthead page.

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Reaction of $Fe(\eta\text{-}C_5H_4)_2S_3$ with $M_3(CO)_{12}$ (M = Ru, Os). Structure of $Fe(\eta\text{-}C_5H_4S)_2Ru_2(CO)_6$ and $Fe(\eta\text{-}C_5H_4S)_2(\mu_3\text{-}S)Os_4(CO)_{11}$

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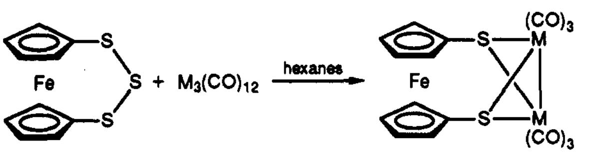
Summary: The thermal reaction of 1,2,3-trithia[3]ferrocenophane (**1**) with $Ru_3(CO)_{12}$ in refluxing hexanes affords the complex $Fe(\eta\text{-}C_5H_4S)_2Ru_2(CO)_6$ (**4**) in moderate yield. The reaction of **1** with $Os_3(CO)_{12}$ yields $Fe(\eta\text{-}C_5H_4S)_2(S)Os_2(CO)_6$ (**5**) in low yield in refluxing cyclohexane and four products in moderate to low yields in refluxing toluene. These compounds were identified as the diosmium species $Fe(\eta\text{-}C_5H_4S)_2Os_2(CO)_6$ (**6**), the triosmium species $Fe(\eta\text{-}C_5H_4S)_2Os_3(CO)_{10}$ (**7**), and the tetraosmium species $Fe(\eta\text{-}C_5H_4S)_2(\mu_3\text{-}S)Os_4(CO)_{11}$ (**8**) and $Fe(\eta\text{-}C_5H_4S)_2(\mu_3\text{-}S)_2Os_4(CO)_{10}$ (**9**). Only complexes **4** and **8** were characterized by using X-ray crystallography. The common sawhorse geometry is found for **4**, with the $Fe(\eta\text{-}C_5H_4S)_2$ group bridging the two $Ru(CO)_3$ moieties. The osmium cluster **8** consists of a μ_3-S ligand bridging a spiked triangle of osmium atoms with the $Fe(\eta\text{-}C_5H_4S)_2$ ligand bridging the spike Os–Os bond. Both structures have eclipsed and nearly parallel cyclopentadienyl rings. Crystals of **4** are monoclinic, with a = 7.685 (3) Å, b = 13.866 (4) Å, c = 18.225 (2) Å, β = 96.43 (2)°, Z = 4, and space group $P2_1/n$, and those of **8** are also monoclinic, with a = 11.872 (2) Å, b = 14.230 (3) Å, c = 16.543 (4) Å, β = 101.20 (2)°, Z = 4, and space group $P2_1/n$. The structures were solved by the Patterson method and were refined by full-matrix least-squares procedures to R = 0.028 and 0.033 for 3773 and 4262 reflections with $I \geq 3\sigma(I)$, respectively.

Bishop and Davison[1a] first reported that ferrocene derivatives with donor atoms in the 1,1′-positions, for example $Fe(\eta\text{-}C_5H_4PPh_2)_2$, can coordinate to some transition metals to give chelate complexes such as $(L\text{-}L)Mo(CO)_4$, and a number of workers have since made contributions to this field.[1]

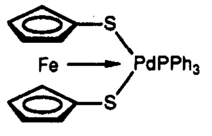
The isolation of 1,2,3-trithia[3]ferrocenophane (1)[2] provided a route to ferrocene-1,1′-dithiol and bidentate dithiolate complexes. A series of 1,3-dithia[3]ferrocenophanes of main-group elements was prepared from the dithiol and the appropriate halide.[3] The reaction of 1 with $Fe_3(CO)_{12}$ afforded 2[4] (eq 1). 1 was also reacted with low-valent, coordinatively unsaturated transition-metal species such as tetrakis(triphenylphosphine)palladium(0). The product proved to be 3, which contains a Fe→Pd bond, rather than the expected dithiolate derivative.[5,6]



(1)

1

2, M = Fe
4, M = Ru



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