Organometallics 1992, *11*, 665–672

secting the diars o-C_6H_4 ring.

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Synthesis, Reactivity, and Structural Characterization of the Dinuclear Zirconocenophane Complexes $[SiMe_2(C_5H_4)_2][(C_5H_5)Zr(\mu\text{-}X)]_2$ (X = S, Cl)

Joseph Cacciola, Karuna P. Reddy, and Jeffrey L. Petersen*

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506-6045

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The treatment of $[SiMe_2(C_5H_4)_2][CpZrH(\mu\text{-}H)]_2$ with elemental sulfur affords the disulfido-bridged dinuclear Zr(IV) complex $[SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}S)]_2$ (1). Ambient photolysis of $[SiMe_2(C_5H_4)_2]$-$[CpZrCl(\mu\text{-}H)]_2$ proceeds with the reductive elimination of H_2 and the formation of the corresponding dichloro-bridged dinuclear Zr(III) complex $[SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}Cl)]_2$ (2). These diamagnetic zirconocenophane compounds have been characterized by ^1H and ^{13}C NMR measurements, electronic spectroscopy, elemental analysis, and X-ray crystallographic methods. Reactivity studies of 1 and 2 with various Lewis bases were used to evaluate the susceptibility of the Zr–(μ-X)–Zr (X = S, Cl) bridges to cleavage. No detectable reaction of 1 with PMe_3, CNMe, or pyridine is observed within the temperature range of 20–130 °C, whereas the addition of PMe_3 or THF to 2 is accompanied by the formation of dinuclear paramagnetic Zr(III) adducts, which have been identified in solution by EPR. The reactions of 2 with $Ph_3P{=}O$ and CO_2 occur with O atom abstraction giving the oxo-bridged species $[SiMe_2(C_5H_4)_2]$-$[CpZrCl]_2(\mu\text{-}O)$. Compounds 1 and 2 both crystallize in a monoclinic lattice of $P2_1/c$ symmetry ($Z = 4$) with unit cell parameters of $a = 17.148$ (5) Å, $b = 8.178$ (2) Å, $c = 15.611$ (4) Å, $\beta = 91.95$ (2)° and $a = 17.126$ (2) Å, $b = 8.098$ (1) Å, $c = 15.624$ (4) Å, $\beta = 91.16$ (2)°, respectively. In each case, the central $Zr_2(\mu\text{-}X)_2$ core is nearly planar with the Zr⋯Zr interatomic separation being 3.5210 (6) and 3.3853 (4) Å in 1 and 2, respectively.

Introduction

The electrophilicity of high-valent bis(cyclopentadienyl)metal complexes of group 4 transition metals has led to their application to many important metal-catalyzed (olefin metathesis,[1] olefin polymerization,[2] ring-opening metathesis polymerization of cyclic olefins,[3] dehydrogenative polymerization of silanes[4]) or metal-assisted (hydrozirconation,[5] C,C-coupling,[6] heteroatom transfer,[7] stereoselective aldol condensation[8]) processes. Although the chemistry of these electron-deficient reagents remains an active area of research activity, far less is known about the chemical potential of dinuclear compounds containing two proximal electron-deficient metallocene centers. To reduce the susceptibility of homodinuclear group 4 metal complexes toward fragmentation, a difunctional ligand capable of stabilizing high metal oxidation states is required. Two ligands that have been successfully used for this purpose are the fulvalene ligand, $C_{10}H_8^{2-}$, and the bridged bis(cyclopentadienyl) ligand, $[X(C_5H_4)_2]^{2-}$.

Fulvalene-bridged dinuclear complexes of Zr have been obtained by several different routes. Herrmann and coworkers[9] observed that Na/Hg amalgam reduction of Cp_2ZrCl_2 in toluene proceeds with ring-coupling to give $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZr(\mu\text{-}Cl)]_2$. Gambarotta and co-workers[10] have prepared this same dinuclear Zr(III) complex by the comproportionation of $Cp_2Zr(PMe_3)_2$ with Cp_2ZrCl_2. More recently, they[11] observed that mild oxidation of an unusual dinuclear ring-bridged compound, $[(\eta^1{:}\eta^5\text{-}C_5H_4)CpZr$-

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$(PMe_3)]_2$, also provides a means of generating a series of related fulvalene-bridged compounds, $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZr(\mu\text{-}X)]_2$, where X = Cl, Br, I, SPh, or PMe_2. Subsequent reactivity studies conducted by Herrmann and his co-workers[12] have shown that $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZr(\mu\text{-}Cl)]_2$ is a potent two-electron reductant, reacting with O_2 ad Cl_2 to give $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZrCl]_2(\mu\text{-}O)$ and $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZrCl_2]_2$, respectively.

Although the fulvalene ligand is capable of coordinating two electrophilic metal centers, its inherent rotational flexibility can lead to either a trans or a cis orientation of the coordinated metal fragments.[11] Another drawback is its potential to undergo carbon–carbon bond cleavage leading to the formation of dinuclear complexes containing $\eta^1{:}\eta^5\text{-}C_5H_4$ bridging groups.[5,13]

We have employed the dimethylsilyl-bridged bis(cyclopentadienyl) dianion, $[SiMe_2(C_5H_4)_2]^{2-}$, as an alternative linking system. In an earlier paper we[14] reported that its dilithio salt reacts metathetically with 2 equiv of $CpZrCl_3{\cdot}2THF$ and $(Cp^*ZrCl_3)_x$, affording $[SiMe_2(C_5H_4)_2][CpZrCl_2]_2$ and $[SiMe_2(C_5H_4)_2][Cp^*ZrCl_2]_2$, respectively. The corresponding dinuclear zirconocenophane hydride complexes $[SiMe_2(C_5H_4)_2][CpZrCl(\mu\text{-}H)]_2$ and $[SiMe_2(C_5H_4)_2][CpZrH(\mu\text{-}H)]_2$ have been prepared[15] and serve, for the purpose of this study, as suitable reagents for the preparation of zirconocenophane complexes containing two single-atom bridges. Specifically, treatment of $[SiMe_2(C_5H_4)_2][CpZrH(\mu\text{-}H)]_2$ with sulfur affords the disulfido-bridged complex $[SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}S)]_2$ (**1**), whereas dinuclear reductive elimination of H_2 from $[SiMe_2(C_5H_4)_2][CpZrCl(\mu\text{-}H)]_2$ upon ambient photolysis yields the diamagnetic chloro-bridged species $[SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}Cl)]_2$ (**2**). X-ray structural determinations of **1** and **2** have enabled us to evaluate how the structural parameters within the $Zr_2(\mu\text{-}X)_2$ core are affected by the introduction of a $SiMe_2$ linkage between the two cyclopentadienyl rings. The susceptibility of the sulfido and chloro groups to convert from bridging to terminal ligands has been explored by reacting $[SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}X)]_2$ (X = S, Cl) with various Lewis bases. The collective results of these studies are discussed and contrasted whenever possible with the related fulvalene-bridged complexes.

Experimental Section

Reagents. Reagents grade solvents were purified using standard methods and freshly distilled under N_2. Toluene, benzene, and pentane were dried over Na/K alloy while tetrahydrofuran was refluxed over potassium benzophenone ketyl; each solvent was stored in a flask containing $[(C_5H_5)_2Ti(\mu\text{-}Cl)_2]_2Zn$.[16] Chlorinated solvents (CCl_4, $CHCl_3$, CH_2Cl_2) were distilled from P_4O_{10}. Starting materials, such as $CpZrCl_3{\cdot}2THF$,[17] $[SiMe_2(C_5H_4)_2][CpZrCl_2]_2$,[14] $[SiMe_2(C_5H_4)_2][CpZrCl(\mu\text{-}H)]_2$,[15] and $[SiMe_2(C_5H_4)_2][CpZrH(\mu\text{-}H)]_2$,[15] were prepared using literature procedures. Dicyclopentadiene (Eastman), zirconocene dichloride (Aldrich or Boulder Scientific), $LiAl(O\text{-}t\text{-}Bu)_3H$ (Aldrich), MeMgBr (Aldrich, 3 M in Et_2O), MeLi (Aldrich, 1.6 M in Et_2O), *n*-BuLi (Aldrich, 1.6 M in hexane), Ph_3PO (Aldrich), and CO_2 (Matheson) were used without further purification. $SiMe_2Cl_2$ (Petrarch) and PMe_3 (Strem) were distilled from 4A molecular sieves prior to use, whereas pyridine (Aldrich) was distilled from BaO. The deuterated solvents, chloroform-d_1 (Aldrich, 99.8%), benzene-d_6 (Aldrich, 99.5%), and toluene-d_8 (Cambridge Isotope Laboratories, 99.6%), were dried over activated molecular sieves prior to use.

Elemental Analyses. Elemental analyses were carried out by Oneida Research Services, Whitesboro, NY.

Instrumentation. ^1H and ^{13}C NMR spectra were recorded using a JEOL GX-270 FT-NMR spectrometer operating in the FT mode at 270 MHz (^1H) or 67.5 MHz (^{13}C). The ^1H chemical shifts (δ) are referenced to the residual proton peaks of toluene-d_8 at δ 2.09 (vs TMS), benzene-d_6 at δ 7.15 (vs TMS), and chloroform-d_1 at δ 7.24 (vs TMS). The ^{13}C resonances are referenced to the central peak of toluene-d_8 at δ 20.4 (vs TMS), chloroform-d_1 at δ 77.0 (vs TMS), and benzene-d_6 at δ 128.0 (vs TMS). Infrared spectra were measured using either KBr disks or matched NaCl plates on a Perkin-Elmer 1600 series FT-IR spectrometer calibrated relative to polystyrene film. Electronic spectra were measured on a Hewlett-Packard Model 8542A diode array spectrometer controlled by a HP UV/vis ChemStation data system. Illumination was provided by a single-beam, low-pressure deuterium lamp with the wavelength monitored by a diode array possessing 2-nm resolution. EPR spectra were measured on an IBM/Bruker ER200-SCR EPR spectrometer controlled by an ASPECT computer system. The microwave frequency was monitored with a Hewlett-Packard 5340A frequency counter. The magnetic field of the spectrometer was calibrated by an internal NMR gaussmeter (±0.01 G).

General Procedure. Due to the air and moisture sensitivity of the organozirconium compounds, all reactions and manipulations were carried out on a double-manifold, high-vacuum line and/or in a Vacuum Atmospheres glovebox. Air- and moisture-sensitive compounds were synthesized using either standard Schlenk techniques or pressure-equalizing swivel filter frits equipped with Teflon stopcocks. Argon and nitrogen were prepurified by passage over activated BTS catalyst and 4A molecular sieves. All glassware was flame-dried under vacuum or oven-dried prior to use. The addition of a stoichiometric amount of a volatile reagent was accomplished with the aid of a calibrated gas bulb fitted with Teflon stopcocks. NMR sample tubes were sealed with a torch under approximately 500 Torr of argon (or N_2). Photolysis was performed in a 16 cm × 3 cm Pyrex tube fitted with a Solv-seal joint and a vacuum stopcock. Irradiation was done with two 275-W sunlamps.

Synthesis of Compounds. Preparation of $[SiMe_2(C_5H_4)_2][CpZrMe_2]_2$. $[SiMe_2(C_5H_4)_2][CpZrCl_2]_2$ (0.600 g, 0.937 mmol) was weighed into a 100-mL Solv-seal flask that was then attached to a swivel filter frit assembly and evacuated. Toluene (ca. 25 mL) was added via vacuum distillation. The reaction flask was then submerged in a liquid nitrogen/acetone slush bath. Under an Ar flush, MeMgBr (3 M, 1.25 mL, 3.75 mmol) was introduced through the side arm with a syringe. The solution was warmed to room temperature and then stirred for several hours. The solution was filtered, the toluene was removed, and the product was washed with pentane (ca. 25 mL) to yield a beige solid, $[SiMe_2(C_5H_4)_2][CpZrMe_2]_2$ (0.450 g, 86%). The absence of any detectable impurities in the solution ^1H and ^{13}C NMR spectra in benzene-d_6 indicated that no further purification was necessary. ^1H NMR: 5.96, 5.94 (t, distal and proximal protons of C_5H_4, $J_{H\text{-}H}$ = 2.6 Hz), 5.75 (s, C_5H_5), 0.33 (s, $SiMe_2$), −0.09 (s, ZrMe). ^{13}C NMR (multiplicity, $^1J_{C\text{-}H}$ in hertz): 128.3 (s, bridgehead C), 117.4, 114.6 (d, distal and proximal carbons of C_5H_4, 171), 110.8 (d, C_5H_5, 172), 31.0 (q, ZrMe, 117), −0.43 (q, SiMe, 119).

Preparation of $[SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}S)]_2$ (1). $[SiMe_2(C_5H_4)_2][CpZrH(\mu\text{-}H)]_2$ (0.360 g, 0.716 mmol) and S_8 (0.100 g, 3.12 mmol of S) were weighed into a 100-mL Solv-seal flask that was attached to a swivel filter frit assembly and evacuated. Toluene (ca. 40 mL) was added via vacuum distillation to the reaction flask. Upon being warmed to room temperature, the reaction proceeded with immediate and vigorous effervescence. Once gas evolution subsided, an atmosphere of argon was introduced into the reaction vessel and the solution was heated overnight at 110 °C. The solution was filtered, the toluene was removed, and the product was washed with pentane (ca. 25 mL), affording a green powder (0.157 g, 39%). This compound was also prepared by heating a toluene solution of $[SiMe_2(C_5H_4)_2][CpZrMe_2]_2$ with a stoichiometric amount of S_8 overnight. The electronic spectrum of a dilute

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toluene (0.142×10^{-4} M) solution of 7 exhibits a single electronic absorption at $\lambda_{max} = 410$ nm with $\epsilon_{max} = 5.66 \times 10^3$ M^{-1} cm^{-1}. ^1H NMR (chloroform-d_1): 6.75, 6.12 (t, distal and proximal protons of C_5H_4, $J_{H-H} = 2.6$ Hz), 6.40 (s, C_5H_5), 0.70 (s, $SiMe_2$). ^{13}C NMR (chloroform-d_1; multiplicity, $^1J_{C-H}$ in hertz): 125.2, 113.1 (d, distal and proximal carbons of C_5H_5, 173), 115.0 (s, bridgehead C), 113.8 (d, C_5H_5, 173), 0.22 (q, SiMe, 118). Anal. Calcd for $C_{22}H_{24}Zr_2S_2Si$: C, 46.93; H, 4.30. Found: C, 46.20; H, 4.01.

Preparation of $[SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}Cl)]_2$ (2). $[SiMe_2(C_5H_4)_2][CpZrCl(\mu\text{-}H)]_2$ (0.502 g, 0.878 mmol) was weighed into a 16 cm × 3 cm Pyrex tube equipped with a Solv-seal adapter that was then attached to a swivel filter frit assembly and evacuated. Toluene (ca. 20 mL) was added to the Pyrex tube via vacuum distillation. After the solution was warmed to room temperature, an atmosphere of argon was introduced into the filter frit assembly. The reaction mixture was irradiated with two 275-W sunlamps for a total of 18 h. The dark red solution was filtered. After the removal of toluene, the product was washed with pentane (ca. 10 mL) to yield a red crystalline product (0.377 g, 75%). The electronic spectrum of a dilute toluene solution (5.89×10^{-6} M) exhibits a single broad electronic absorption at 474 nm with ϵ_{max} of 1.3×10^4 M^{-1} cm^{-1}. ^1H NMR (benzene-d_6): 5.43, 5.28 (t, distal and proximal protons of C_5H_4, $J_{H-H} = 2.6$ Hz), 5.20 (s, C_5H_5), 0.09 (s, $SiMe_2$); ^{13}C NMR (benzene-d_6; multiplicity, $^1J_{C-H}$ in hertz): 114.3 (s, bridgehead C), 112.4, 104.2 (d, distal and proximal carbons of C_5H_4, 165), 103.3 (d, C_5H_5, 170), –0.66 (q, SiMe, 120). Anal. Calcd for $C_{22}H_{24}Zr_2Cl_2Si$: C, 46.37; H, 4.25. Found: C, 47.00; H, 4.51.

Reactivity Studies. Small-scale reactions of 1 and 2 were conducted in sealed NMR tubes prepared by adding a stoichiometric amount of a solid or volatile reagent (with the aid of a calibrated gas bulb) to a solution of the dinuclear zirconocenophane compound. The reactions of 1 with CH_3CN, pyridine, and PMe_3 and the reactions of 2 with THF, PMe_3, CN-*t*-Bu, $Ph_3P{=}O$, and CO_2 were carried out in this manner.

X-ray Diffraction Data Collection. The same general procedure was employed to collect the X-ray diffraction data for $[SiMe_2(C_5H_4)_2][(C_5H_5)Zr(\mu\text{-}X)]_2$ (X = Cl, S). In each case, a suitable crystalline sample was obtained by cleavage of a larger crystal and then sealed in a glass capillary tube under a prepurified N_2 atmosphere. Each sample was optically aligned on a Picker goniostat which is operated by a Krisel Control diffractometer automation system. Following a search for low-angle diffraction peaks ($5° < 2\theta < 10°$), the orientation angles for several intense reflections were used by an autoindexing algorithm[18] to determine preliminary cell constants. The orientation angles (ω, χ, 2θ) for 20 higher order reflections ($35° < 2\theta < 40°$) were optimized by an automatic peak-centering routine[19] and least-squares fit to provide the refined lattice parameters (Table I) and the orientation matrix. The systematic absences uniquely determined the space group to be $P2_1/c$ for both compounds.

Intensity data ($\pm hkl$) were measured at 21 °C with Zr-filtered Mo Kα X-ray radiation at a takeoff angle of 2°. A θ–2θ scan mode was employed with a fixed scan rate of 2°/min and a variable scan width of $1.1 + 0.9 \tan\theta$. The intensities of three standard reflections were measured every 90 min of exposure time and gave no indication of significant sample decomposition. The integrated intensity I and its standard deviation $\sigma_c(I)$ for each reflection were calculated from the expressions $I = \omega(S/t_s - B/t_b)$ and $\sigma_c(I) = (S/t_s^2 + B/t_b^2)^{1/2}$, where S is the total scan count measured in time t_s and B is the combined background count in time t_b. The intensity data were corrected for absorption and Lorentz–polarization effects. The standard deviation of the square of each structure factor, $F_o^2 = AI/Lp$, was calculated from $\sigma(F_o^2) = [\sigma_c(F_o^2)^2 + (0.025F_o^2)^2]^{1/2}$. Symmetry-related reflections were averaged. Further details regarding the cell constants and data collection parameters are summarized in Table I.

Table I. Data for the X-ray Diffraction Analyses of $[SiMe_2(C_5H_4)_2][(C_5H_5)Zr(\mu\text{-}X)]_2$ (X = Cl, S)

	X = Cl	X = S
A. Crystal Data		
crystal system	monoclinic	monoclinic
space group	$P2_1/c$ (C_{2h}^5, No. 14)	$P2_1/c$ (C_{2h}^5, No. 14)
a, Å	17.126 (2)	17.148 (5)
b, Å	8.098 (1)	8.178 (2)
c, Å	15.624 (4)	15.611 (4)
β, deg	91.16 (2)	91.95 (2)
V, Å^3	2166.3 (7)	2187.9 (1.0)
fw	569.87	563.08
d(calcd), g/cm^3	1.747	1.709
Z	4	4
μ, cm^{-1}	12.46	11.74
cryst dimens, mm	0.25 × 0.35 × 0.375	0.250 × 0.215 × 0.425
B. Data Collection and Structural Analysis		
reflcns sampled	$\pm hkl$ ($5° < 2\theta < 55°$)	$\pm hkl$ ($5° < 2\theta < 50°$)
% crystal decay	0	2
total no. of measd reflcns	5201	4102
no. of unique data used ($F_o^2 > 0.0$)	5012	3872
agreement between equiv data		
$R_{av}(F_o)$	0.025	0.029
$R_{av}(F_o^2)$	0.013	0.024
transmission coeff	0.65–0.75	0.75–0.79
discrepancy indices for data with $F_o^2 > \sigma(F_o^2)$		
$R(F_o)$	0.042	0.054
$R(F_o^2)$	0.040	0.064
$R_w(F_o^2)$	0.069	0.097
σ_1	1.64	2.38
no. of variables	341	340
data to parameter ratio	14.7:1	11.4:1

Structural Analyses and Refinements. Initial coordinates for the two Zr and two Cl atoms in $[SiMe_2(C_5H_4)_2][(C_5H_5)Zr(\mu\text{-}Cl)]_2$ and the two Zr and two S atoms in $[SiMe_2(C_5H_4)_2][(C_5H_5)Zr(\mu\text{-}S)]_2$ were provided by the corresponding E map calculated on the basis of the phases assigned by MULTAN78[20] for the solution with the highest figure of merit. Positions for the remaining non-hydrogen atoms were obtained by Fourier methods and refined with anisotropic thermal parameters. All of the hydrogen atoms were located on the subsequent difference Fourier map which was calculated using only low-angle data with $(\sin\theta)/\lambda < 0.40$ Å^{-1} and then refined with isotropic thermal parameters. An examination of the agreement between the observed and calculated structure factors near the end of the structural refinement of $[SiMe_2(C_5H_4)_2][(C_5H_5)Zr(\mu\text{-}Cl)]_2$ indicated that several strong reflections suffered from extinction effects. An isotropic extinction coefficient g was introduced into the refinement. No extinction correction was deemed necessary for the refinement of the X-ray diffraction data of $[SiMe_2(C_5H_4)_2][(C_5H_5)Zr(\mu\text{-}S)]_2$. Full-matrix refinement (based on F_o^2)[21-25] of the positional and thermal parameters for the 27 non-hydrogen and 24 hydrogen atoms converged with final discrepancy indices of $R(F_o) = 0.042$, $R(F_o^2) = 0.040$, $R_w(F_o^2) = 0.069$, $\sigma_1 = 1.64$, and $g = (0.17(2)) \times 10^{-5}$ for the 4366 reflections with $F_o^2 > \sigma(F_o^2)$ for $[SiMe_2(C_5H_4)_2][(C_5H_5)Zr(\mu\text{-}Cl)]_2$ and with values of $R(F_o) = 0.054$, $R(F_o^2) = 0.064$, $R_w(F_o^2) = 0.097$, and $\sigma_1 = 2.38$ for the 3314 reflections with $F_o^2 > \sigma(F_o^2)$ for $[SiMe_2(C_5H_4)_2][(C_5H_5)Zr(\mu\text{-}S)]_2$. A final difference Fourier map verified the completeness of each structural refinement.[26]

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(19) This peak-centering algorithm is similar to that described by Busing: Busing, W. R. *Crystallographic Computing*; Ahmed, F. R., Ed.; Munksgaard: Copenhagen, 1970; p 319. The ω, χ, and 2θ angles were optimized with respect to the $K_{\alpha 1}$ peak ($\lambda = 0.709\,26$ Å).

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(21) The least-squares refinement[22] of the X-ray diffraction data was based upon the minimization of $\sum w_i|F_o^2 - S^2F_c^2|^2$, where w_i is the individual weighting factor and S is the scale factor. The discrepancy indices were calculated from the expressions $R(F_o^2) = \sum||F_o| - |F_c||/\sum|F_o|$, $R(F_o^2) = \sum|F_o^2 - F_c^2|$, and $R_w(F_o^2) = [\sum w_i|F_o^2 - F_c^2|^2/\sum w_iF_o^4]^{1/2}$. The standard deviation of an observation of unit weight σ_1 equals $[\sum w_i|F_o^2 - F_c^2|/(n - p)]^{1/2}$, where n is number of observations and p is the number of parameters varied during the last refinement cycle.

(22) The scattering factors employed in all of the structure factor calculations were those of Cromer and Mann[23] for the non-hydrogen atoms and those of Stewart et al.[24] for the hydrogen atoms with corrections included for anomalous dispersion.[25]

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(24) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(25) Cromer, D. T.; Liberman, D. J. *J. Chem. Phys.* **1970**, *53*, 1891.

Table II. Positional Parameters for All of the Atoms in $[SiMe_2(C_5H_4)_2][(C_5H_5)Zr(\mu\text{-}Cl)]_2$[a]

atom	*x*	*y*	*z*
Zr1	0.29557 (1)	−0.13747 (3)	0.28565 (2)
Zr2	0.26989 (2)	0.14737 (3)	0.44115 (2)
Cl1	0.28849 (4)	−0.16744 (8)	0.44914 (4)
Cl2	0.27783 (4)	0.17800 (9)	0.27765 (4)
Si	0.08246 (4)	−0.08021 (11)	0.36348 (5)
C1	0.1507 (2)	−0.1745 (3)	0.2860 (2)
C2	0.1856 (2)	−0.3345 (4)	0.2909 (2)
C3	0.2225 (2)	−0.3669 (5)	0.2143 (3)
C4	0.2120 (2)	−0.2309 (5)	0.1604 (2)
C5	0.1678 (2)	−0.1146 (4)	0.2031 (2)
C6	0.1271 (2)	0.0857 (4)	0.4293 (2)
C7	0.1357 (2)	0.2573 (4)	0.4104 (2)
C8	0.1627 (2)	0.3413 (4)	0.4832 (2)
C9	0.1705 (2)	0.2242 (5)	0.5499 (2)
C10	0.1496 (2)	0.0701 (4)	0.5181 (2)
C11	0.0494 (2)	−0.2443 (5)	0.4372 (3)
C12	−0.0006 (3)	0.0103 (7)	0.3010 (3)
C13	0.4028 (2)	−0.3392 (5)	0.2570 (3)
C14	0.4310 (2)	−0.2450 (5)	0.3231 (3)
C15	0.4400 (2)	−0.0847 (5)	0.2944 (3)
C16	0.4185 (2)	−0.0805 (6)	0.2071 (3)
C17	0.3958 (2)	0.2403 (7)	0.1851 (3)
C18	0.3602 (2)	0.3873 (5)	0.4596 (3)
C19	0.4067 (2)	0.2663 (5)	0.4251 (3)
C20	0.4132 (2)	0.1384 (6)	0.4834 (3)
C21	0.3705 (2)	0.1811 (6)	0.5557 (3)
C22	0.3390 (3)	−0.3368 (6)	0.5410 (3)
H1	0.187 (2)	−0.412 (4)	0.337 (2)
H2	0.249 (2)	−0.456 (4)	0.204 (2)
H3	0.233 (2)	−0.228 (5)	0.106 (2)
H4	0.150 (2)	−0.016 (4)	0.182 (2)
H5	0.126 (2)	0.302 (4)	0.356 (2)
H6	0.180 (2)	0.459 (5)	0.491 (2)
H7	0.188 (2)	0.240 (4)	0.605 (2)
H8	0.151 (2)	−0.027 (4)	0.550 (2)
H9	0.030 (2)	−0.336 (5)	0.403 (3)
H10	0.015 (2)	−0.213 (5)	0.480 (2)
H11	0.089 (3)	−0.293 (6)	0.463 (3)
H12	0.013 (3)	0.087 (6)	0.266 (3)
H13	−0.029 (3)	−0.075 (6)	0.275 (3)
H14	−0.043 (3)	0.061 (5)	0.333 (3)
H15	0.388 (2)	−0.457 (5)	0.262 (2)
H16	0.439 (2)	−0.277 (4)	0.374 (2)
H17	0.459 (2)	−0.005 (5)	0.328 (3)
H18	0.422 (2)	−0.006 (4)	0.170 (3)
H19	0.378 (2)	−0.280 (5)	0.135 (2)
H20	0.344 (2)	0.489 (5)	0.435 (3)
H21	0.428 (2)	0.275 (5)	0.375 (2)
H22	0.435 (2)	0.060 (5)	0.480 (3)
H23	0.365 (3)	0.110 (6)	0.605 (3)
H24	0.304 (3)	0.403 (6)	0.578 (3)

[a] The esd's in parentheses for this and all subsequent tables refer to the least significant figures.

Table III. Positional Parameters for All of the Atoms in $[SiMe_2(C_5H_4)_2][(C_5H_5)Zr(\mu\text{-}S)]_2$

atom	*x*	*y*	*z*
Zr1	0.29790 (2)	−0.14706 (6)	0.28751 (3)
Zr2	0.27300 (3)	0.15305 (6)	0.44598 (3)
S1	0.29244 (7)	−0.14935 (17)	0.44627 (7)
S2	0.28573 (8)	0.15666 (17)	0.28804 (8)
Si	0.08375 (8)	−0.07918 (19)	0.36456 (9)
C1	0.1492 (3)	−0.1776 (6)	0.2867 (3)
C2	0.1817 (3)	−0.3362 (7)	0.2926 (4)
C3	0.2191 (3)	−0.3726 (9)	0.2171 (4)
C4	0.2118 (3)	−0.2382 (9)	0.1630 (4)
C5	0.1680 (3)	−0.1202 (8)	0.2043 (3)
C6	0.1265 (3)	0.0876 (6)	0.4319 (3)
C7	0.1362 (3)	0.2563 (7)	0.4114 (3)
C8	0.1639 (4)	0.3404 (7)	0.4836 (4)
C9	0.1707 (3)	0.2254 (9)	0.5516 (4)
C10	0.1492 (3)	0.0742 (8)	0.5203 (3)
C11	0.0509 (4)	−0.2428 (10)	0.4383 (5)
C12	0.0009 (5)	0.0108 (15)	0.3012 (6)
C13	0.3996 (3)	−0.3586 (9)	0.2575 (4)
C14	0.4322 (3)	−0.2664 (8)	0.3230 (4)
C15	0.4458 (3)	−0.1091 (9)	0.2938 (4)
C16	0.4225 (3)	−0.1025 (11)	0.2079 (5)
C17	0.3949 (4)	−0.2576 (12)	0.1849 (4)
C18	0.3609 (5)	0.3959 (10)	0.4687 (6)
C19	0.4099 (4)	0.2716 (14)	0.4402 (6)
C20	0.4127 (4)	0.1510 (13)	0.5028 (7)
C21	0.3665 (5)	0.2097 (12)	0.5690 (5)
C22	0.3382 (4)	0.3574 (13)	0.5469 (5)
H1	0.180 (3)	−0.405 (6)	0.337 (3)
H2	0.242 (4)	−0.450 (7)	0.204 (4)
H3	0.226 (3)	−0.231 (7)	0.115 (3)
H4	0.154 (3)	−0.030 (6)	0.184 (3)
H5	0.127 (3)	0.311 (6)	0.358 (3)
H6	0.178 (3)	0.463 (8)	0.493 (4)
H7	0.183 (3)	0.244 (8)	0.605 (4)
H8	0.149 (2)	−0.029 (5)	0.552 (3)
H9	0.032 (4)	−0.335 (9)	0.404 (4)
H10	0.016 (4)	−0.209 (9)	0.472 (5)
H11	0.088 (4)	−0.277 (9)	0.472 (4)
H12	0.016 (4)	0.099 (8)	0.264 (4)
H13	−0.012 (6)	−0.057 (12)	0.282 (7)
H14	−0.040 (6)	0.051 (11)	0.317 (6)
H15	0.370 (4)	−0.488 (8)	0.264 (4)
H16	0.445 (3)	−0.299 (7)	0.372 (3)
H17	0.466 (3)	−0.027 (6)	0.329 (3)
H18	0.423 (4)	−0.010 (7)	0.170 (4)
H19	0.377 (3)	−0.300 (8)	0.139 (4)
H20	0.346 (4)	0.483 (8)	0.437 (5)
H21	0.426 (4)	0.289 (9)	0.397 (4)
H22	0.420 (4)	0.056 (10)	0.511 (5)
H23	0.361 (4)	0.147 (9)	0.610 (5)
H24	0.304 (4)	0.446 (9)	0.574 (5)

The positional parameters for all of the atoms of $[SiMe_2(C_5H_4)_2][(C_5H_5)Zr(\mu\text{-}X)]_2$ are given in Table II for X = Cl and Table III for X = S. Selected interatomic distances and bond angles and their esd's are compared for the non-hydrogen atoms in Table IV for these two compounds. Tables of refined thermal parameters, all interatomic distances and angles, the equations of pertinent least-squares planes and their dihedral angles, and tables of the observed and calculated structure factors are available as supplementary material.

Discussion of Results

Synthesis and Characterization of $[SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}S)]_2$. Herrmann and co-workers[27] reported that the fulvalene-bridged dinuclear Ti(III) hydride complex $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpTi(\mu\text{-}H)]_2$ readily undergoes electrophilic attack by elemental sulfur, resulting in the oxidation of the metal and the formation of the disulfido-bridged titanocene species $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpTi(\mu\text{-}S)]_2$ in good yield. The addition of S_8 to a solution of $[SiMe_2(C_5H_4)_2][CpZrH(\mu\text{-}H)]_2$ similarly proceeds with the liberation of H_2S and the formation of the deep green disulfido complex $[SiMe_2(C_5H_4)_2][CpZrS]_2$ (1) (eq 1). Compound

$$[SiMe_2(C_5H_4)_2][CpZrH(\mu\text{-}H)]_2 + {}^1\!/_2S_8 \rightarrow 2H_2S + [SiMe_2(C_5H_4)_2][CpZrS]_2 \quad (1)$$

1 can be obtained alternatively by refluxing a toluene solution of $[SiMe_2(C_5H_4)_2][CpZrMe_2]_2$ in the presence of sulfur for 12 h (eq 2). Gambarotta and co-workers[11]

$$[SiMe_2(C_5H_4)_2][CpZrMe_2]_2 + {}^1\!/_2S_8 \rightarrow 2Me_2S + [SiMe_2(C_5H_4)_2][CpZrS]_2 \quad (2)$$

prepared $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZr(\mu\text{-}S)]_2$ in a similar fashion by reacting S_8 with *trans*-$[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZrMe_2]_2$. Whereas Gambarotta and co-workers reported that this reaction proceeds vigorously at room temperature, reaction 2 does

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(26) The computer programs that were used for the X-ray diffraction data analyses are described in: Nicholson, G. A.; Petersen, J. L.; McCormick, B. J. *Inorg. Chem.* **1980**, *19*, 195.

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Table IV. Interatomic Distances (Å) and Bond Angles (deg) for the Non-Hydrogen Atoms in $[SiMe_2(C_5H_4)_2][(C_5H_5)Zr(\mu\text{-}X)]_2$ (X = Cl, S)[a,b]

	X = Cl	X = S
	A. Interatomic Distances	
Zr1–X1	2.5711 (7)	2.481 (1)
Zr1–X2	2.5754 (8)	2.493 (1)
Zr2–X1	2.5719 (7)	2.495 (1)
Zr2–X2	2.5728 (7)	2.483 (1)
Zr1···Cp(1)	2.197 (4)	2.240 (7)
Zr1···Cp(3)	2.214 (5)	2.236 (5)
Zr2···Cp(2)	2.194 (4)	2.235 (8)
Zr2···Cp(4)	2.209 (5)	2.232 (5)
Zr1···Zr2	3.3853 (4)	3.5210 (6)
X1···X2	3.875 (1)	3.515 (2)
range Zr–C distances	2.471 (3)–2.551 (4)	2.503 (6)–2.571 (5)
range Si–C distances	1.849 (3)–1.863 (3)	1.855 (9)–1.865 (5)
range C–C distances	1.364 (6)–1.437 (4)	1.332 (12)–1.427 (8)
	B. Bond Angles	
X1–Zr1–X2	97.70 (2)	89.90 (4)
Cp(1)–Zr1–Cp(3)	127.9 (2)	127.0 (2)
Zr1–X1–Zr2	82.33 (2)	90.01 (4)
X1–Zr2–X2	97.74 (2)	89.85 (4)
Cp(2)–Zr2–Cp(4)	128.0 (2)	125.8 (3)
Zr1–X2–Zr2	82.23 (2)	90.10 (5)
C1–Si–C6	113.7 (1)	116.8 (4)
C1–Si–C11	108.2 (2)	107.1 (3)
C1–Si–C12	107.6 (2)	106.9 (3)
C6–Si–C11	107.7 (2)	107.4 (3)
C6–Si–C12	108.0 (2)	106.9 (4)
C11–Si–C12	111.7 (2)	111.8 (4)
Si–C1–C2	127.2 (2)	127.5 (4)
Si–C1–C5	126.6 (2)	126.8 (4)
Si–C6–C7	129.4 (2)	129.0 (4)
Si–C6–C10	125.0 (2)	125.5 (4)
range of C–C–C angles	105.4 (3)–109.4 (3)	105.1 (5)–109.7 (5)

[a] Cp(*n*) denotes the centroid of a cyclopentadienyl ring. Cp(1), Cp(2), Cp(3), and Cp(4) contain carbon atoms C1–C5, C6–C10, C13–C17, and C18–C22, respectively. [b] The esd's for the interatomic distances and bond angles were calculated from the standard errors of the fractional coordinates of the corresponding atomic positions.

not occur to any appreciable extent until a temperature of 110 °C is obtained. This noticeable difference in reaction rates is probably a consequence of the different molecular structures of these dinuclear zirconocenophane methyl compounds. $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZrMe_2]_2$[11] adopts a trans geometry, which makes the methyl groups more accessible for reaction with sulfur. In contrast, the cis arrangement of the zirconocene units in $[SiMe_2(C_5H_4)_2][CpZrMe_2]_2$ produces a more crowded environment about each Zr center, thus requiring a higher activation energy to initiate the reaction.

The ^1H NMR spectrum of 1 is characterized by the presence of singlets at δ 0.70 and 6.40 due to the dimethylsilyl and Cp ring protons, respectively. A pair of pseudotriplets are observed at δ 6.12 and 6.75 for the distal and proximal protons of the bridging Cp rings. The possibility of 1 being a μ-SH-bridged species was ruled out by the absence of any other proton resonances. In the ^{13}C NMR spectrum, the corresponding carbon resonances are represented by a quartet at δ 0.22 ($^1J_{C-H}$ 118 Hz) and three sets of doublets located at δ 113.8 ($^1J_{C-H}$ 173 Hz), 113.1 ($^1J_{C-H}$ 173 Hz), and 125.2 ($^1J_{C-H}$ 173 Hz). The quarternary bridgehead carbon appears as a low-intensity singlet at δ 115.0. The electronic spectrum of 1 is characterized by a strong absorption band at $\lambda = 410$ nm ($\epsilon = 5.66 \times 10^3$ M^{-1} cm^{-1}) consistent with a ligand to metal charge-transfer band probably due to electron transfer from a filled S p_π orbital to an empty Zr d_π orbital.

The coordination chemistry of the sulfide ligand has been studied extensively with both terminal and bridging modes of coordination being prevalent. For 1, the sulfido groups could adopt one of three possible modes of coordination: terminal, asymmetrically bridging, or symmetrically bridging. A single-crystal X-ray structural analysis of 1 (vide infra) confirmed that the two sulfido groups bridge the Zr centers in a symmetrical manner.

Reactivity Studies of $[SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}S)]_2$. Bergman and co-workers[28] recently described the preparation of the monomeric zirconocene sulfide complex $Cp^*_2Zr{=}S(Py)$ by the dehydrohalogenation of $Cp^*_2ZrI(SH)$ in the presence of pyridine. An X-ray crystal structure determination confirmed the presence of a Zr=S bond in this complex. The Zr—S distance of 2.316 (1) Å is significantly shorter than a Zr—S single bond, which can range from 2.42 to 2.72 Å[29,30] depending on the metal coordination number and the types of ancillary ligands present. A chemical consequence of the π bond between the sulfide and the Zr in $Cp^*_2Zr{=}S(Py)$ is its ability to undergo [2 + 2] cycloaddition of substituted acetylenes (eq 3). The bridging mode of the sulfido ligands in 1 inhibits

$$Cp^*_2Zr{=}S(Py) + RC{\equiv}CR \rightarrow$$
$$Cp^*_2\overline{ZrSC(R){=}C}(R) + C_5H_5N \quad (3)$$

similar cycloaddition reactions from occurring with alkynes. However, the addition of a suitable Lewis base may make it possible to convert the bridging (σ-bonded) sulfido ligands of 1 to terminal (π-bonded) sulfides, thereby enhancing the reactivity of 1 toward alkynes. Separate NMR samples containing solutions of 1 and PMe_3, CNMe, or pyridine were heated initially at 30 °C in an oil bath, and their ^1H NMR spectra were measured daily. The temperature of the oil bath was raised in 10 °C increments and the process repeated until a final temperature of 130 °C was reached. Conversion of the bridging sulfides to terminally bound ligands following metal coordination of a Lewis base should proceed with the appearance of four distinct multiplets for the ring protons of the bridging bis(cyclopentadienyl) ligand as chirality is introduced at each Zr center. ^1H NMR measurements furnished no evidence for the formation of a PMe_3, CNMe, or pyridine adduct of 1 (eq 4). The observed resistance of the sulfido bridges to cleavage is a consequence of their symmetric mode of coordination.

$$[SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}S)]_2 + 2X \not\rightarrow$$
$$[SiMe_2(C_5H_4)_2][CpZr{=}S(X)]_2 \quad (4)$$
$$X = PMe_3,\ CNMe,\ C_5H_5N$$

Photolytic Generation of $[SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}Cl)]_2$. Trivalent zirconium complexes are much less common in zirconocene chemistry.[31] The susceptibility of Zr(III) compounds toward air oxidation and the lack of convenient routes for their preparation have hindered initial efforts to develop their chemistry.

The binuclear Zr(III) complex $[SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}Cl)]_2$ (2) was originally prepared by Reddy and Petersen[15] from $[SiMe_2(C_5H_4)_2][CpZrCl(\mu\text{-}H)]_2$ by heating this dinuclear Zr hydride complex under an atmosphere of ethylene for 4 days at 100 °C. This reaction proceeds with the

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Table V. Interatomic Distances (Å) and Bond Angles (deg) for Various Dinuclear Zirconium Complexes Containing μ-Cl and μ-S Ligands

compound	Zr⋯Zr	Zr–X	Zr–X–Zr	X–Zr–X	fold angle	ref
$[SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}Cl)]_2$	3.3853 (4)	2.5711 (7) 2.5719 (7) 2.5728 (7) 2.5754 (8)	82.33 (2) 82.23 (2)	97.70 (2) 97.74 (2)	0.5	this work
$[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZr(\mu\text{-}Cl)]_2$	3.233 (1)	2.568 (2) 2.571 (2) 2.583 (2) 2.591 (2)	77.6 (1) 77.7 (1)	99.5 (1) 100.5 (1)	21.0	10
$[SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}S)]_2$	3.5210 (6)	2.481 (1) 2.483 (1) 2.493 (1) 2.495 (1)	90.01 (4) 90.10 (5)	89.85 (4) 89.90 (4)	4.1	this work
$[Cp_2Zr(\mu\text{-}S)]_2$	3.530 (2)	2.482 (3) 2.490 (3)	90.4 (1)	89.6 (1)	0	29
$[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZr(\mu\text{-}S)]_2$	3.4154 (5)	2.487 (1) 2.493 (1)	86.60 (3)	87.85 (1)	35.2	11

evolution of ethane and results in a modest yield of **2**. A significantly higher yield of **2** is obtained by ambient photolysis of a toluene solution of $[SiMe_2(C_5H_4)_2][CpZrCl(\mu\text{-}H)]_2$ (eq 5). The electronic spectrum of a toluene solution of **2** exhibits a single broad absorption at 474 nm with an extinction coefficient of 1.3 × 10^4 M^{-1} cm^{-1}, consistent with a charge-transfer band.

$$[SiMe_2(C_5H_4)_2][CpZrCl(\mu\text{-}H)]_2 \xrightarrow{h\nu} H_2 + [SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}Cl)]_2 \quad (5)$$

Despite the fact that each Zr center in **2** is formally trivalent, the ^1H and ^{13}C NMR spectra indicate that **2** is diamagnetic. Its ^1H NMR spectrum displays the usual singlet for both the bridging dimethylsilyl group (δ 0.09) and the Cp ring protons (δ 5.20) with a pair of pseudotriplets for the distal and proximal protons on the bridging Cp rings located at δ 5.28 and 5.43, respectively. In the ^{13}C NMR spectrum, the dimethylsilyl carbons appear as a quartet (δ −0.66, $^1J_{C-H}$ 120 Hz) and the resonances of the Cp ring carbons and the distal and proximal carbons of the bridging ligand appear as doublets located at δ 103.3 ($^1J_{C-H}$ 170 Hz), 104.2 ($^1J_{C-H}$ 165 Hz), and 112.4 ($^1J_{C-H}$ 165 Hz), respectively. A low-intensity singlet located at δ 114.3 is assigned to the bridgehead carbon. The diamagnetism observed for **2** suggests that its structure is analogous to that of $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZr(\mu\text{-}Cl)]_2$ which contains two chloro bridges. An X-ray structural determination of **2** was conducted to confirm its structure and to evaluate the influence of the $SiMe_2$ linkage on the Zr⋯Zr separation and the conformational structure of the Zr_2Cl_2 moiety.

Description of the Molecular Structures of $[SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}X)]_2$ (X = S, Cl). The molecular structures of **1** and **2** have been determined by X-ray diffraction methods. Both compounds crystallize in a monoclinic unit cell with similar lattice dimensions. Their solid-state structures are well-behaved; perspective views of their molecular configurations are displayed in Figures 1 and 2, respectively, with the appropriate atom-labeling schemes. In each case, the $[SiMe_2(C_5H_4)_2]^{2-}$ ligand coordinates in a bridging fashion by linking two $(C_5H_5)ZrX$ units in a cis orientation. The pseudotetrahedral ligand arrangement about each Zr center is compatible with that exhibited by numerous canted Cp_2ZrL_2-type complexes.[32] The two zirconocene centers are further joined by two single-atom bridges to produce a nearly planar $Zr_2(\mu\text{-}X)_2$ core.

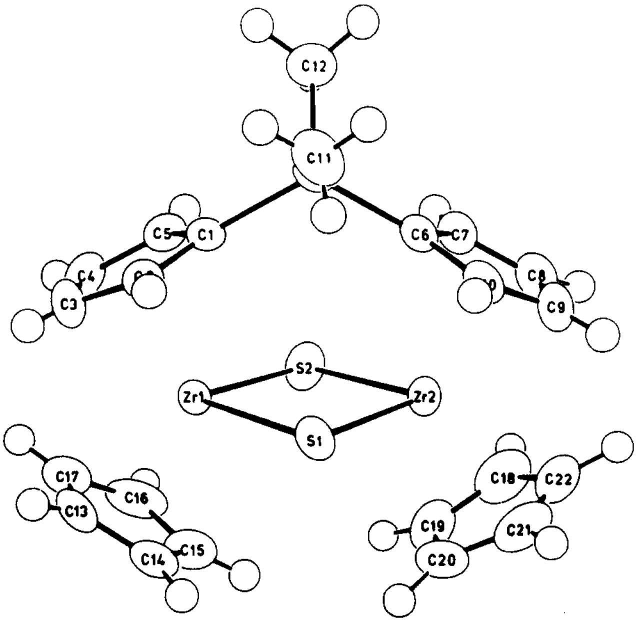

Figure 1. Perspective view of the molecular structure of $[SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}S)]_2$ with the atom-labeling scheme for the non-hydrogen atoms. The thermal ellipsoids are scaled to enclose 50% probability. The radii of the spheres for the hydrogen atoms have been set arbitrarily for clarity.

The overall molecular structures of **1** and **2** are analogous to those reported by Gambarotta and co-workers[10,11] for the corresponding dinuclear fulvalene-bridged $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZr(\mu\text{-}X)]_2$ complexes. However, it is apparent from the structural information summarized in Table V that the presence of the $SiMe_2$ group between the cyclopentadienyl rings has a significant effect on the structural parameters within the four-membered Zr_2X_2 core. The resultant increase in the distance between the ring centroids of the linked cyclopentadienyl rings consistently leads to a lengthening of the Zr⋯Zr separation and reduces the folding of the Zr_2X_2 ring along the X⋯X vector.

The structural parameters within the $\overline{\text{ZrSZrS}}$ core of **1** are remarkably similar to those reported by Bottomley and co-workers[29] for $[Cp_2Zr(\mu\text{-}S)]_2$. In both cases, the central four-membered ring constitutes a nearly perfect square with sides of essentially equal length and 90° internal angles. The Zr–S distances of 2.49 Å (av) imply the presence of some double-bond character, presumably due to electron donation from the filled pπ orbitals on S to the empy a_1 orbital on each zirconocene fragment. Replace-

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[32] Representative examples include: (a) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr., Sec. B* **1974**, *B30*, 2290. (b) Jeffrey, J.; Lappert, M. F.; Loung-Thi, N. T.; Webb, M.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1981**, 1953 and references cited therein. (c) Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Pentilla, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750.

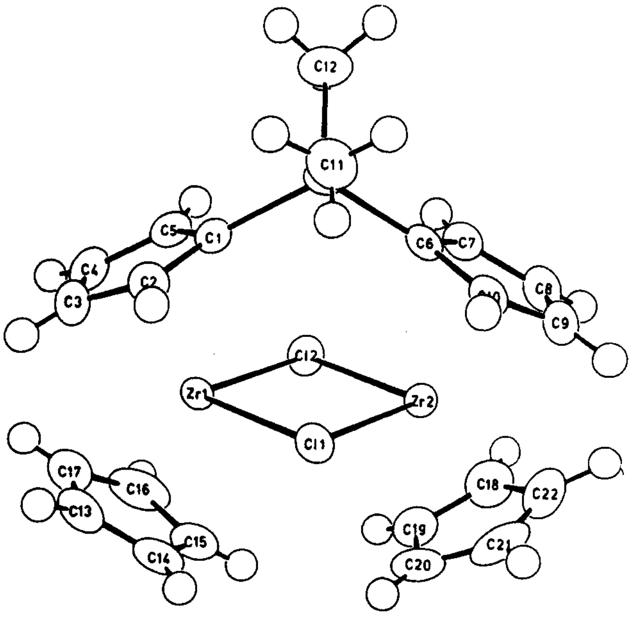

Figure 2. Perspective view of the molecular configuration of $[SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}Cl)]_2$ with the atom-labeling scheme for the non-hydrogen atoms. The same level of scaling was employed here as in Figure 1.

ment of the fulvalene ligand of $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZr(\mu\text{-}S)]_2$ with $[SiMe_2(C_5H_4)_2]^{2-}$ produces a ca. 40° change in the acute dihedral angle between the planar cyclopentadienyl ligands and is accompanied by a comparable decrease in the folding of the Zr_2S_2 core. This modification further leads to a 0.11-Å increase in the Zr···Zr separation from 3.4154 (5) Å in $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZr(\mu\text{-}S)]_2$[11] to 3.5210 (6) Å in $[SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}S)]_2$. Comparable structural changes are observed also for the corresponding chloro-bridged Zr(III) species.

The diamagnetism exhibited by $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZr(\mu\text{-}Cl)]_2$[10] and 2 can be rationalized by invoking the presence of a direct Zr–Zr bond. This explanation is supported by extended Hückel and ab initio SCF/CI calculations conducted by Rohmer and Benard[33] on related dinuclear Zr(III) complexes $[Cp_2Zr(\mu\text{-}I)]_2$, $[ZrCl_3(PH_3)_2]_2$, and $[Cp_2Zr(\mu\text{-}PH_2)]_2$. The HOMO is described as a Zr–Zr σ-bonding orbital with A_g symmetry. Although their calculations suggest that through-space metal–metal coupling may exist up to an intermetallic separation of 4.25 Å, the Zr–Zr distances in the mechanically linked dinuclear complex $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZr(\mu\text{-}Cl)]_2$ and 2 are primarily a consequence of the structural constraints imposed by the bridging chloro and linked bis(cyclopentadienyl) ligands and may not reflect a significant difference in the degree of metal–metal d-orbital overlap. The ca. 0.15-Å shorter Zr–Zr distance of 3.233 (1) Å in $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZr(\mu\text{-}Cl)]_2$ compared to that of 3.3853 (4) Å in 2 reflects the greater puckering of the Zr_2Cl_2 ring in the former case. The metal–metal interaction arises from the overlap of two hybridized metal orbitals that are directed primarily along the normal of the plane that bisects each Cl–Zr–Cl angle (Figure 3). MO calculations[34] carried out on d^0 Cp_2ML_2 complexes indicate that the relative contributions of the d_{z^2} and $d_{x^2-y^2}$ AOs to this hybridized metal orbital are influenced by the size of the L–M–L angle. Increasing this angle leads to a redistribution of the metal orbital character, with a greater orbital contribution being directed along the line bisecting the L–M–L angle. Upon extending this correlation to the two d^1 Zr(III) centers of $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZr(\mu\text{-}Cl)]_2$ and 2, one would anticipate that a significant orbital interaction along the Zr–Zr axis should mandate a substantial increase in the Cl–Zr–Cl bond angles. However, any variation in the internal angles within the Zr_2Cl_2 core is moderated by the presence of the chloro bridges. As a result, the Cl–Zr–Cl bond angles in these dinuclear zirconocenophane complexes are less than 15° larger than the acute Cl–Nb–Cl angle of 84.6 (1)° in the corresponding d^1 mononuclear niobocene complex Cp_2NbCl_2.[35] The rather long Zr–Cl distances of 2.57–2.59 Å reflect the presence of an antibonding interaction involving the in-plane Cl p π orbitals. In contrast, the average Zr···Cp (centroid) distance of 2.20 Å falls within the range of values observed for the majority of complexes containing a canted zirconocene moiety.[32] Although the structure of the Zr_2Cl_2 core supports the presence of a metal–metal bond, the orbital overlap associated with this interaction is modest.

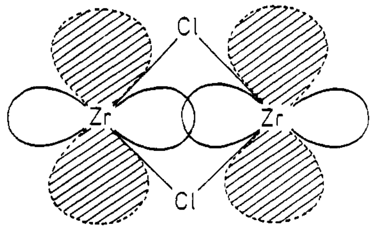

Figure 3. Pictorial representation of the metal d-orbital overlap associated with the Zr–Zr bonding interaction.

Preliminary Reactivity Studies of $[SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}Cl)]_2$. Reactivity studies were also performed to determine if the Zr–Cl bonds of 2 could be severed by the addition of a Lewis base such as PMe_3, THF, or CN-*t*-Bu. ^1H NMR measurements revealed that the reaction of 2 with PMe_3 or THF proceeds at room temperature with a gradual decrease in the intensity of the proton resonances of 2 relative to the residual solvent resonance. Parallel solution EPR measurements indicate that these reactions proceed with the formation of paramagnetic Zr(III) species. The solution EPR spectrum of 2, following the addition of THF, exhibits a single strong resonance centered at $g = 1.968$. The g value is consistent with the value of 1.970 reported by Samuel and co-workers[31b] for the related mononuclear Zr(III) species $Cp_2ZrCl(THF)$. This result indicates that the addition of THF to a solution of 2 is accompanied by cleavage of its chloro bridges yielding a paramagnetic Zr(III) adduct, presumably $[SiMe_2(C_5H_4)_2][CpZrCl(THF)]_2$ (eq 6). The

$$[SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}Cl)]_2 + 2THF \rightarrow [SiMe_2(C_5H_4)_2][CpZrCl(THF)]_2 \quad (6)$$

solution EPR spectrum of 2 in the presence of PMe_3 is characterized by an intense 1:1 doublet and several weaker satellite resonances. The doublet centered at $g = 1.982$ is attributed to hyperfine coupling of the magnetic moment of an unpaired electron with the nuclear magnetic moment of a coordinated phosphine ligand ($A(^{31}P) = 14.3$ G). The weaker satellite resonances are due to ^{91}Zr hyperfine coupling ($A(^{91}Zr) = 20.0$ G). The values of these magnetic parameters compare well with those reported by Samuel and co-workers[31b] for the Zr(III) adduct $Cp_2ZrCl(PMe_3)$, for which $g = 1.979$, $A(^{31}P) = 17.5$ G, and $A(^{91}Zr) = 23.0$ G. The observance of ^{31}P hyperfine coupling strongly

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[33] Rohmer, M.-M.; Benard, M. *Organometallics* **1991**, *10*, 157.

[34] (a) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. (b) Petersen, J. L.; Lichtenberger, D. L.; Fenske, R. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6433.

[35] Green, J. C.; Green, M. L. H.; Prout, C. K. *J. Chem. Soc., Chem. Commun.* **1972**, 421.

supports the formulation of the paramagnetic product as the dinuclear Zr(III) phosphine adduct $[SiMe_2(C_5H_4)_2][CpZrCl(PMe_3)]_2$ (eq 7). Unfortunately, this species shows limited stability in solution.

$$[SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}Cl)]_2 + 2PMe_3 \rightarrow [SiMe_2(C_5H_4)_2][CpZrCl(PMe_3)]_2 \quad (7)$$

Whereas the reactions of 2 with THF and PMe_3 occur with the gradual formation of paramagnetic Zr(III) adducts, the corresponding reaction of 2 with CN-*t*-Bu proceeds quite differently. This reaction occurs with the consumption of 1 equiv of CN-*t*-Bu, giving a bright orange product. Its NMR and IR spectra[36] are compatible with the formation of a dinuclear complex containing a semibridging isocyanide ligand similar to that observed in the fulvalene-bridged complex $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZrCl]_2(\sigma,\pi\text{-CN-}t\text{-Bu})$, reported by Herrmann and co-workers.[29]

Although the reaction of 2 with various Lewis bases results in the cleavage of the chloro bridges, two different types of dinuclear products are observed. For PMe_3 and THF, metal coordination to each Zr center leads to the formation of dinuclear zirconocenophane species containing two mechanically linked paramagnetic zirconocene fragments. Alternatively, the unsaturation introduced by the CN triple bond of CN-*t*-Bu enables it to coordinate in both a σ and π fashion.

The presence of two Zr(III) centers in $[SiMe_2(C_5H_4)_2][CpZr(\mu\text{-}Cl)]_2$ suggests that this compound should behave as a two-electron reductant. Evidence of this behavior is provided by the reactions of 2 with stoichiometric amounts of either Ph_3PO or CO_2. Heating the corresponding reaction mixture in a sealed NMR tube at 75 °C similarly proceeds with O atom abstraction and complete conversion of 2 to $[SiMe_2(C_5H_4)_2][CpZrCl]_2(\mu\text{-}O)$[14] within several days. For Ph_3PO, the formation of Ph_3P is readily apparent from the NMR spectrum. The formation of two strong Zr–O bonds provides the thermodynamic driving force for cleavage of the P=O bond (130 kcal/mol)[37] in Ph_3PO and a C=O bond (127 kcal/mol)[38] of CO_2. The formation of the oxo-bridge compound clearly requires the participation of both Zr(III) centers.

Future work will focus on modifying the structures of 1 and 2 in an effort to make the Zr–(μ-X)–Zr (X = S, Cl) linkages more susceptible to cleavage and thereby enhance the reactivity. By replacing Cp with Cp*, the additional steric bulk of Cp* should increase the Zr···Zr separation and reduce the ability of the bridging atoms to interact symmetrically with both zirconium centers.

Acknowledgment. Support for this research was provided in part by the West Virginia Energy and Water Research Center and the Petroleum Research Fund, administered by the American Chemical Society. Computer time for the X-ray structural analyses was made available by the West Virginia Network for Educational Telecomputing.

Registry No. 1, 138234-09-0; **2**, 118920-58-4; $[SiMe_2(C_5H_4)_2][CpZrCl_2]_2$, 118920-56-2; $[SiMe_2(C_5H_4)_2][CpZrMe_2]_2$, 138234-10-3; $[SiMe_2(C_5H_4)_2][CpZrH(\mu\text{-}H)]_2$, 118920-55-1; $[SiMe_2(C_5H_4)_2][CpZrCl(\mu\text{-}H)]_2$, 118920-54-0; $[SiMe_2(C_5H_4)_2][CpZrCl(THF)]_2$, 138234-11-4; $[SiMe_2(C_5H_4)_2][CpZrCl(PMe_3)]_2$, 138234-12-5; $[SiMe_2(C_5H_4)_2][CpZrCl]_2(\mu\text{-}O)$, 118920-57-3.

Supplementary Material Available: Tables of thermal parameters, interatomic distances and bond angles, and least-squares planes for the X-ray structural analyses of $[SiMe_2(C_5H_4)_2][(C_5H_5)Zr(\mu\text{-}X)]_2$ (X = S, Cl) (15 pages); listings of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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[36] Spectroscopic data for $[SiMe_2(C_5H_4)_2][CpZrCl]_2(\sigma,\pi\text{-CN-}t\text{-Bu})$: ^1H NMR (C_6D_6) δ 6.59, 6.58, 5.93 (2 H), 5.83, 5.78, 5.68, 4.68 (m, C_5H_4), 5.97, 5.64 (s, C_5H_5), 1.38 (s, CMe_3), 0.44, 0.16 (s, SiMe); $^{13}C\{^1H\}$ NMR (C_6D_6) 129.5, 127.1, 126.3, 122.5, 115.9, 115.4, 114.6, 107.7, 106.7, 106.2 (C_5H_4), 110.2, 109.7 (C_5H_5), 66.9 (*C*Me), 29.7 (C*Me*$_3$), 0.36, 0.02 (SiMe); IR $\nu_{C=N}$ = 1600 cm^{-1}.

[37] Cobridge, D. E. C. *Phosphorous*; Elsevier Scientific Publishing: Oxford, 1978; p 24.

[38] Atkins, P. W. *Physical Chemistry*, 3rd ed.; W. H. Freeman: New York, 1986; p 821.

Reactions of Hydrosilanes and Olefins in the Presence of Cp_2MCl_2/nBuLi

Joyce Y. Corey* and Xiao-Hong Zhu

Department of Chemistry, University of Missouri—St. Louis, St. Louis, Missouri 63121

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The Cp_2MCl_2/nBuLi (M = Ti, Zr, Hf) catalyzed reactions of $PhMeSiH_2$ in the presence of near-stoichiometric quantities of cyclic and acyclic olefins have demonstrated a range of reactions including hydrosilylation of the olefin, isomerization/hydrosilation of internal olefins, dehydrocoupling of the silane to silicon oligomers, and dehydrocoupling of the silane with the olefin to form vinylsilanes. The product which dominates is a function of the metal and the nature of the olefin. Hydrosilation of terminal acyclic olefins and isomerization/hydrosilylation of internal olefins occur with M = Zr. Cyclic olefins promote the formation of silicon oligomers, and cyclooctene and norbornene with M = Ti provide the highest conversion and highest rates, respectively. Dehydrocoupling of the vinyl hydrogen in cyclooctene and the hydrosilane occurs when M = Zr or Hf. The variations in chemistry can be rationalized through the silylmetal, $Cp_2M(H)SiPhMeH$, and plausible mechanisms for formation of the various products are discussed.

Introduction

We have demonstrated recently that the combination Cp_2MCl_2/nBuLi (M = Ti, Zr, Hf) provides a catalyst system effective for the condensation of secondary silanes to oligomers.[1] In the case of $PhMeSiH_2$, disilane through octasilane are obtained in the presence of Cp_2ZrCl_2 and 2 equiv of *n*BuLi when the reaction is conducted at 90 °C

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[1] Corey, J. Y.; Zhu, X.-H.; Bedard, T. C.; Lange, L. D. *Organometallics* 1991, *10*, 924.

0276-7333/92/2311-0672$03.00/0