# Binuclear Zirconium(III) and Zirconium(IV) Complexes: Mild Oxidation of Low-Valent Zirconium as a Synthetic Pathway to a Class of Tri- and Tetravalent Zirconium Fulvalene Complexes. Molecular Structures of [η⁵:η⁵-C₁₀H₈][CpZrSPh]₂, [η⁵:η⁵-C₁₀H₈][CpZr(CH₃)₂]₂, and [η⁵:η⁵-C₁₀H₈][CpZr]₂[μ-S]₂

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The oxidation of [CpZr(PMe₃)(η¹:η⁵-C₅H₄)]₂ (1) with several reagents (R₃PX₂ (R = n-Bu, Me; X = Cl, Br, I), PhSSPh, Me₂PPMe₂) afforded the reductive coupling of the two bridging η¹:η⁵-C₅H₄ rings. The reaction allowed the large-scale preparation of a class of fulvalene-containing cis-Zr(III) [η⁵:η⁵-C₁₀H₈][CpZrX]₂ (X = Cl (3), Br (4), I (5), SPh (6), PMe₂ (7)) and trans-Zr(IV) [η⁵:η⁵-C₁₀H₈][CpZrX₂]₂ (X = Cl (8), I (9), SPh (10), Me (11)) complexes with respect to the plane of the fulvalene ligand. The cis-(fulvalene)Zr(IV) complex [η⁵:η⁵-C₁₀H₈][CpZrS]₂ (12) was obtained upon treatment of 1, 6, or 11 with S₈. Crystal data for 6, 11, and 12 are as follows: 6, C₃₂H₂₈Zr₂S₂, monoclinic, space group P2₁/n, with a = 9.929 (1) Å, b = 16.017 (1) Å, c = 16.641 (1) Å, β = 97.67 (1)°, Z = 4, and R = 0.031 (R_w = 0.031); 11, C₂₄H₃₀Zr₂, orthorhombic, space group Pca2₁, with a = 14.694 (1) Å, b = 11.381 (1) Å, c = 13.026 (2) Å, Z = 4, and R = 0.058 (R_w = 0.064); 12, C₂₀H₁₈Zr₂S₂, orthorhombic, space group Fdd2, with a = 22.523 (2) Å, b = 20.446 (2) Å, c = 8.001 (1) Å, Z = 8, and R = 0.023 (R_w = 0.025). A double-carbonylation reaction of 11 led to the formation of the binuclear bis(acyl) derivative [η⁵:η⁵-C₁₀H₈][CpZrMe(COMe)]₂.

## Introduction

The direct coupling of the two cyclopentadienyl rings to form a fulvalene dianion allows, in principle, the formation of a large class of binuclear compounds. The most attractive characteristic of the fulvalene dianion as a ligand is its ability to constrain short contacts between the two metals (up to the metal–metal bond range),[1] giving considerable potential for modeling the interactions of organic molecules with metal surfaces,[2] for probing the interactions between the two metals (M–M bond, magnetic coupling),[3] and for understanding the bi- and polymetallic activation of organic substrates.[4] Another attractive feature is the steric flexibility provided by the rotational freedom of the two rings along the C–C linkage, enabling the dinuclear complex to accommodate any value of the intermetallic distance (from 2.8 up to 4.7 Å) that might be convenient for the bimetallic activation of a substrate. This free rotation is somewhat moderated by the electronic conjugation between the two rings, as apparent from the solid-state structures of the stable complexes, which show only two main rotameric configurations (cis and trans) of the two metal centers with respect to the planar fulvalene. On the other hand, although quite relevant, this limitation imposes some steric restrictions, which might be determinant for the stereoselectivity of the bimetallic activation. Finally, fulvalene dianion as a ligand obviously retains the prominent and desirable characteristics of the cyclopentadienyl rings in terms of stabilization of the metal center, with the additional advantage of a decreased possibility of involvement in chemical transformations.

In spite of these promising features and wide interest in them, the chemistry of the fulvalene-containing systems is poorly developed, probably due to the limited availability of synthetic pathways.[5] The methodologies available,

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(4) As examples: (a) Wilson, R. D.; Bau, R. *J. Am. Chem. Soc.* 1976, 98, 4687. (b) Tachikama, M.; Shapley, J. R.; Haltiwanger, R. C.; Pierpont, C. G. *J. Am. Chem. Soc.* 1976, 98, 4651. (c) Thomas, M. G.; Muetterties, E. L.; Day, R. O.; Day, V. W. *J. Am. Chem. Soc.* 1976, 98, 4645.

(5) Four general synthetic procedures have been reported: (i) reaction of low-valent transition-metal complexes with dihydrofulvalene;[6] (ii) reductive coupling between halocyclopentadienyl rings;[7] (iii) reaction of transition-metal halides with fulvalene dianion;[8] (iv) deprotonation/oxidation of monocyclopentadienyl systems.[9]

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although successful in several cases, are generally hampered by difficulties including the instability of dihydrofulvalene, small-scale accessibility, and limited availability of suitable starting materials. In addition, for some systems none of these methods is viable as, for instance, in the chemistry of zirconium, where bimetallic complexes are especially desirable for metal-promoted organic synthesis.

The ability of $\eta^1:\eta^5$-bonded cyclopentadienyl rings to form fulvalene via reductive coupling has been recognized in several cases,[1b,10] in particular during attempts to prepare low-valent metallocenes.[11] However, in spite of the apparent generality, it has never been developed into a rational and useful synthetic method.

In this paper we wish to describe the oxidation under mild conditions of $[CpZr(PMe_3)(\eta^1:\eta^5-C_5H_4)]_2$ (1), which allows the preparation of a class of Zr(III) and Zr(IV) fulvalene compounds via reductive coupling of the two bridging cyclopentadienyl rings.

## Experimental Part

All the operations were performed under a dry nitrogen atmosphere with use of standard Schlenk-tube techniques or in a nitrogen-filled drybox (Braun MB200). $PMe_3$,[12] $Me_2PPMe_2$,[13] and $[CpZr(PMe_3)(\eta^1:\eta^5-C_5H_4)]_2$[14] (1) were prepared according to published procedures. $R_3PX_2$ (R = $n$-Bu, Me; X = Cl, Br, I) was prepared by addition of pure halogen to a solution of the phosphine in pentane, and the resulting white solids were used without further purification. PhSSPh, $Bu_3P$, and $S_8$ (Aldrich) were used without further purification. Solvents used for magnetic resonance were vacuum-transferred from Na/K alloy (benzene-$d_6$, THF-$d_8$) or dried over 4-Å molecular sieves (pyridine-$d_5$, DMSO-$d_6$). $^1H$ and $^{13}C$ NMR spectra were recorded on Varian VXR300 and Bruker WH90 spectrometers. Chemical shifts are reported in $\delta$ units referenced to tetramethylsilane and calculated from the position of the solvent resonance. Solutions for NMR-tube experiments were prepared inside the drybox with use of an analytical balance. CO-absorption experiments were carried out in NMR tubes connected to a high-vacuum line equipped with a Toepler pump for the addition of the desired amounts of carbon monoxide. Elemental analyses were carried out at the Chemistry Department of the University of Groningen.

**Preparation of $[\eta^5:\eta^5-C_{10}H_8][CpZrX]_2$ (X = Cl (3), Br (4)).** In a standard experiment a toluene solution (50 mL) of $[CpZr(PMe_3)(\eta^1:\eta^5-C_5H_4)]_2$ (2.4 g, 4.0 mmol) was reacted with an equimolar amount of $Bu_3PX_2$ (X = Cl, Br). The mixture was stirred and boiled for a few minutes, and the resulting deep red

solution was concentrated to small volume. Emerald green crystals separated upon cooling at -30 °C (yield 68% and 60% for 3 and 4, respectively). Anal. Calcd (found) for $C_{20}H_{18}Zr_2Cl_2$ (3): C, 46.97 (47.20); H, 3.54 (3.70); Zr, 35.61 (35.30); Cl, 13.89 (13.60). Calcd (found) for $C_{20}H_{18}Zr_2Br_2$ (4): C, 40.00 (39.97); H, 2.99 (2.90); Zr, 30.33 (30.00); Br, 27.00 (27.12). NMR data for 3: $^1H$ (300 MHz, benzene-$d_6$, 25 °C) $\delta$ 5.58 (s, 10 H, Cp), 4.94 (pseudo t, 4 H, fulvalene), 3.99 (pseudo t, 4 H, fulvalene); $^{13}C$ (75 MHz, benzene-$d_6$, 25 °C) $\delta$ 102.6 (d, $J_{C-H}$ = 176.1 Hz, Cp), 102.5 (d, $J_{C-H}$ = 176.1 Hz, fulvalene), 99.0 (d, $J_{C-H}$ = 171.5 Hz, fulvalene). No resonance attributable to the quaternary carbon was observed. NMR data for 4: $^1H$ (300 MHz, benzene-$d_6$, 25 °C) $\delta$ 5.58 (s, 10 H, Cp), 4.80 (pseudo t, 4 H, fulvalene), 4.02 (pseudo t, 4 H, fulvalene); $^{13}C$ (75 MHz, benzene-$d_6$, 25 °C) $\delta$ 102.3 (d, $J_{C-H}$ = 176.1 Hz, Cp), 101.8 (d, $J_{C-H}$ = 176.1 Hz, fulvalene), 98.4 (d, $J_{C-H}$ = 171.5 Hz, fulvalene), 97.7 (s, fulvalene).

**Preparation of $[(\eta^1:\eta^5-C_5H_4)CpZrI(PMe_3)]_2$ (2a).** A toluene solution (50 mL) of 1 (2.0 g, 3.4 mmol) was reacted with a stoichiometric amount of $Bu_3PI_2$. A dark red, highly insoluble, microcrystalline solid precipitated upon standing overnight at room temperature (2.2 g, 2.6 mmol, 76% yield). The very low solubility in the common inert organic solvents prevented NMR characterization. Anal. Calcd (found) for $C_{13}H_{18}ZrPI$: C, 36.87 (36.79); H, 4.25 (4.23); Zr, 21.51 (21.49); I, 30.02 (30.00).

**Preparation of $[\eta^5:\eta^5-C_{10}H_8][CpZrI]_2$ (5).** A toluene suspension (200 mL) of 2a (2.5 g, 2.9 mmol) was boiled, and the solvent was allowed to distill out from the reaction mixture through a 20-cm Vigreux column. Neat toluene was added dropwise to the mixture during the distillation to keep the volume constant. The insoluble solid slowly dissolved, forming a deep purple solution. When all the solid had disappeared, the distillation and the addition of toluene was interrupted and the resulting purple solution was concentrated to small volume. Emerald green crystals of 5 separated upon cooling overnight at -30 °C (1.3 g, 1.9 mmol, 65% yield). Anal. Calcd (found) for $C_{20}H_{18}Zr_2I_2$: C, 34.58 (34.57); H, 2.59 (2.57); Zr, 26.22 (26.20); I, 36.60 (36.58). $^1H$ NMR (300 MHz, benzene-$d_6$, 25 °C): $\delta$ 5.61 (s, 10 H, Cp), 4.58 (pseudo t, 4 H, fulvalene), 4.18 (pseudo t, 4 H, fulvalene). $^{13}C$ NMR (75 MHz, benzene-$d_6$, 25 °C): $\delta$ 101.0 (d, $J_{C-H}$ = 175.0 Hz, fulvalene), 100.2 (d, $J_{C-H}$ = 172.7 Hz, Cp), 97.7 (s, fulvalene), 97.5 (d, $J_{C-H}$ = 170.4 Hz, fulvalene).

**Preparation of $[(\eta^1:\eta^5-C_5H_4)CpZrSPh]_2$ (2b).** A toluene solution (250 mL) of 1 (2.1 g, 3.6 mmol) was allowed to react with PhSSPh (0.8 g, 3.6 mmol) at room temperature. The color slowly turned light yellow and light yellow crystalline 2b separated (1.4 g, 2.1 mmol, 59% yield) upon standing overnight at room temperature. Anal. Calcd (found) for $C_{16}H_{14}ZrS$: C, 58.36 (58.33); H, 4.25 (4.22); Zr, 27.66 (27.60); S, 9.72 (9.69). $^1H$ NMR (300 MHz, THF-$d_8$, 25 °C): $\delta$ 7.22 (m, 4 H, phenyl), 7.14 (m, 4 H, phenyl), 7.05 (m, 2 H, phenyl), 6.54 (m, 2 H, $\eta^1:\eta^5$-Cp), 6.36 (m, 2 H, $\eta^1:\eta^5$-Cp), 6.14 (m, 2 H, $\eta^1:\eta^5$-Cp), 5.96 (s, 10 H, Cp), 5.28 (m, 2 H, $\eta^1:\eta^5$-Cp). The instability of the complex in THF together with the poor solubility prevented the recording of $^{13}C$ NMR spectra.

Upon concentration and cooling of the mother liquor of the reaction mixture, a light yellow crystalline solid separated out, which was identified as $[\eta^5:\eta^5-C_{10}H_8][CpZr(SPh)_2]_2$ (10; 0.5 g, 0.8 mmol, 25% yield) (see below).

**Preparation of $[\eta^5:\eta^5-C_{10}H_8][CpZrSPh]_2$ (6).** The reaction took place at room temperature by dissolving 2b (1.64 g, 2.5 mmol) in pyridine (30 mL). The solution turned immediately red, and shiny red crystals of 6 separated at room temperature (0.8 g, 1.2 mmol, 49% yield). Anal. Calcd (found) for $C_{16}H_{14}ZrS$: C, 58.36 (58.33); H, 4.25 (4.22); Zr, 27.66 (27.61); S, 9.72 (9.69). $^1H$ NMR (300 MHz, THF-$d_8$, 25 °C): $\delta$ 7.29–7.03 (m, 10 H, phenyl), 5.93 (s, 10 H, Cp), 5.49 (pseudo t, 4 H, fulvalene), 3.73 (pseudo t, 4 H, fulvalene). $^{13}C$ NMR (75 MHz, THF-$d_8$, 25 °C): $\delta$ 149.0 (s, phenyl), 131.7 (d, $J_{C-H}$ = 158.9 Hz, phenyl), 128.8 (d, $J_{C-H}$ = 158.9 Hz, phenyl), 125.4 (d, $J_{C-H}$ = 161.1 Hz, phenyl), 107.9 (s, fulvalene), 101.8 (d, $J_{C-H}$ = 172.6 Hz, Cp), 98.9 (d, $J_{C-H}$ = 177.2 Hz, fulvalene), 98.3 (d, $J_{C-H}$ = 179.6 Hz, fulvalene).

**Preparation of $[\eta^5:\eta^5-C_{10}H_8][CpZr(PMe_2)]_2$ (7).** A toluene solution (80 mL) of 1 (1.3 g, 2.1 mmol) was reacted with $Me_2PPMe_2$ (0.3 g, 2.8 mmol) at 100 °C for 3 days. The resulting brown solution was concentrated to small volume. Brown crystalline 7 was obtained upon cooling at -30 °C (0.5 g, 0.9 mmol, 43% yield). Anal. Calcd (found) for $C_{12}H_{15}ZrP$: C, 51.24 (51.20);

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H, 5.34 (5.30); Zr, 32.38 (32.15). $^1$H NMR (300 MHz, benzene-$d_6$, 25 °C): $\delta$ 5.19 (s, 10 H, Cp), 4.60 (pseudo t, 4 H, fulvalene), 4.07 (m, 4 H, fulvalene), 1.24 (pseudo t, 6 H, PMe$_2$), 1.12 (pseudo t, 6 H, PMe$_2$). $^{13}$C NMR (75 MHz, benzene-$d_6$, 25 °C): $\delta$ 95.5 (d, $J_{C-H}$ = 170.4 Hz, Cp), 93.3 (d, $J_{C-H}$ = 161.2 Hz, fulvalene), 84.6 (d, $J_{C-H}$ = 179.6 Hz, fulvalene), 21.8 (q, $J_{C-H}$ = 128.9 Hz, Me), 18.0 (q, $J_{C-H}$ = 131.2 Hz, Me). No resonance attributable to the quaternary carbon atom was observed.

**Preparation of [$\eta^5$:$\eta^5$-C$_{10}$H$_8$][CpZrX$_2$]$_2$ (X = Cl (8), I (9)).** In a standard experiment a toluene solution (250 mL) of 1 (3.2 g, 5.4 mmol) was reacted with 2 equiv of Bu$_3$PX$_2$. The solution rapidly turned colorless and white solid 8 (or bright yellow 9) precipitated (yield 78% and 82% for 8 and 9, respectively). The solid was insoluble in the most common organic solvents. A solution suitable for NMR spectroscopy was obtained in DMSO, giving broad resonances before a slow decomposition took place. Anal. Calcd (found) for C$_{10}$H$_9$ZrCl$_2$: C, 41.24 (41.19); H, 3.09 (3.03); Zr, 31.27 (31.19); Cl 24.40 (24.39). Calcd (found) for C$_{10}$H$_9$ZrI$_2$: C, 25.31 (25.30); H, 1.90 (1.88); Zr, 19.20 (19.17); I, 53.58 (53.53).

**Preparation of [$\eta^5$:$\eta^5$-C$_{10}$H$_8$][CpZr(SPh)$_2$]$_2$ (10).** A pyridine solution (100 mL) of 6 (4.0 g, 6.1 mmol) was reacted with PhSSPh (2.7 g, 12.2 mmol). The resulting bright yellow solution was evaporated to dryness and the residual solid redissolved in toluene. Bright yellow crystals of 10 were isolated upon cooling at −30 °C (2.5 g, 2.8 mmol, 46% yield). Anal. Calcd (found) for C$_{12}$H$_{10}$ZrS$_2$: C, 46.60 (46.58); H 3.23 (3.19); Zr, 29.45 (29.39); S, 20.71 (20.69). $^1$H NMR (300 MHz, THF-$d_8$, 25 °C): $\delta$ 7.51 (pseudo d, 4 H, phenyl), 7.23 (pseudo t, 4 H, phenyl), 7.10 (pseudo t, 2 H, phenyl), 6.35 (pseudo t, 4 H, fulvalene), 5.98 (pseudo t, 4 H, fulvalene), 5.76 (s, 10 H, Cp). $^{13}$C NMR (75 MHz, THF-$d_8$, 25 °C): $\delta$ 146.5 (s, phenyl), 133.5 (d, $J_{C-H}$ = 163.4 Hz, phenyl), 128.8 (d, $J_{C-H}$ = 159.0 Hz, phenyl), 125.6 (d, $J_{C-H}$ = 161.3 Hz, phenyl), 119.7 (s, fulvalene), 113.5 (d, $J_{C-H}$ = 175.0 Hz, fulvalene), 113.1 (d, $J_{C-H}$ = 175.0 Hz, fulvalene), 110.0 (d, $J_{C-H}$ = 182.0 Hz, fulvalene).

**Preparation of [$\eta^5$:$\eta^5$-C$_{10}$H$_8$][CpZr(CH$_3$)$_2$]$_2$ (11).** A solution of MeLi in ether (4.5 mL, 2 M) was added dropwise to a toluene suspension (100 mL) of 8 (2.5 g, 4.3 mmol). The solid slowly dissolved during the slow addition at room temperature. After filtration, concentration, and cooling at −30 °C, colorless crystals of 11 separated (1.0 g, 2.0 mmol, 46% yield). Anal. Calcd (found) for C$_{24}$H$_{30}$Zr$_2$: C, 57.54 (57.89); H, 6.04 (6.07); Zr, 36.42 (36.37). $^1$H NMR (300 MHz, benzene-$d_6$, 25 °C): $\delta$ 5.93 (pseudo t, 4 H, fulvalene), 5.75 (s, 10 H, Cp), 5.60 (pseudo t, 4 H, fulvalene), −0.09 (s, 12 H, CH$_3$). $^{13}$C NMR (75 MHz, benzene-$d_6$, 25 °C): $\delta$ 119.5 (s, fulvalene), 109.8 (d, $J_{C-H}$ = 172.7 Hz, Cp), 108.0 (d, $J_{C-H}$ = 170.3 Hz, fulvalene), 106.5 (d, $J_{C-H}$ = 170.3 Hz, fulvalene), 30.5 (q, $J_{C-H}$ = 117.5 Hz, CH$_3$).

**Preparation of [$\eta^5$:$\eta^5$-C$_{10}$H$_8$][CpZrS]$_2$ (12).** A THF solution (100 mL) of 1 (2.3 g, 3.9 mmol) was reacted with S$_8$ (0.5 g, 15.5 mmol). The solution turned light red, and light red crystals of 12 separated upon standing at room temperature (0.9 g, 1.8 mmol, 40% yield). Anal. Calcd (found) for C$_{10}$H$_9$ZrS: C, 47.62 (47.59); H, 3.57 (3.55); Zr, 36.11 (36.09); S, 12.70 (13.04). $^1$H NMR (300 MHz, pyridine-$d_5$, 25 °C): $\delta$ 6.46 (s, 10 H, Cp), 6.40 (pseudo t, 4 H, fulvalene), 6.20 (pseudo t, 4 H, fulvalene). $^{13}$C NMR (75 MHz, pyridine-$d_5$, 25 °C): $\delta$ 113.4 (d, $J_{C-H}$ = 168.1 Hz, fulvalene), 110.8 (d, $J_{C-H}$ = 175.1 Hz, Cp), 106.1 (d, $J_{C-H}$ = 174.9 Hz, fulvalene). No resonance attributable to the quaternary carbon atom was observed.

**Preparation of [$\eta^5$:$\eta^5$-C$_{10}$H$_8$][$\mu$-O][CpZr(CH$_3$)]$_2$ (13).** A toluene solution (30 mL) of 11 (1.0 g, 1.9 mmol) was reacted with 1 equiv of H$_2$O (34 $\mu$L, 1.9 mmol). The resulting solution was boiled for a few minutes, cooled, filtered, and concentrated to small volume. White crystals of 13 separated upon cooling at −80 °C (0.4 g, 0.9 mmol, 46% yield). Anal. Calcd (found) for C$_{22}$H$_{24}$Zr$_2$O: C, 54.38 (54.76); H, 5.17 (5.07); Zr, 37.39 (36.96). $^1$H NMR (300 MHz, benzene-$d_6$, 25 °C): $\delta$ 6.95 (broad s, 2 H, fulvalene), 6.55 (broad s, 2 H, fulvalene), 6.21 (s, 10 H, Cp), 5.94 (broad s, 2 H, fulvalene), 5.67 (broad s, 2 H, fulvalene), 0.74 (s, 6 H, CH$_3$). $^{13}$C NMR (75 MHz, benzene-$d_6$, 25 °C): $\delta$ 110.8 (d, $J_{C-H}$ = 170.3 Hz, fulvalene), 109.8 (d, $J_{C-H}$ = 172.7 Hz, Cp), 108.9 (d, $J_{C-H}$ = 170.3 Hz, fulvalene), 107.5 (d, $J_{C-H}$ = 170.0 Hz, fulvalene), 98.7 (d, $J_{C-H}$ = 168.2 Hz), fulvalene), 17.8 (q, $J_{C-H}$ = 117.4 Hz, CH$_3$).

**Reaction of 11 with CO.** A colorless solution of 11 (0.4 g, 0.8 mmol) in toluene (10 mL) was exposed to an excess of CO. After

filtration of the resulting light yellow solution, pale yellow microcrystalline 15 separated upon standing 2 days at −80 °C (0.13 g, 0.24 mmol, 30% yield). Anal. Calcd (found) for C$_{13}$H$_{15}$ZrO: C, 56.11 (56.09); H, 5.39 (5.33); Zr, 32.73 (32.66). IR (Nujol, KBr, cm$^{-1}$): $\nu_{COMe}$ 1540 (vs), 1130 (vs). $^1$H NMR (300 MHz, benzene-$d_6$, 25 °C): $\delta$ 5.38 (broad m, 8 H, fulvalene), 5.28 (s, 10 H, Cp), 2.20 (s, 3 H, MeCO), 2.19 (s, 3 H, MeCO), 0.50 (s, 3 H, Me), 0.48 (s, 3 H, Me). $^{13}$C NMR (75 MHz, benzene-$d_6$, 25 °C): $\delta$ 318.1 (s, C(O)Me), 317.8 (s, C(O)Me), 106.0 (Cp), 105.8 (Cp), 105.3, 105.2, 104.9, 104.5, 104.2, 103.3, 100.3, 100.1 (fulvalene), 32.2 (COMe), 32.1 (COMe), 14.6 (Me), 14.3 (Me).

**Structure Determination of 6.** X-ray data were collected (100 K) on an Enraf-Nonius CAD4-F diffractometer (Zr-filtered Mo K$\alpha$ radiation) from a dark red block-shaped crystal, sealed in a Lindemann glass capillary. Crystal data and numerical details of the structure determination are given in Table I. Unit cell parameters and their standard deviations were determined from a least-squares treatment of the SET4 setting angles of 25 reflections in the range 14 < $\theta$ < 18°. The space group was determined from the observed systematic extinctions. There was no decay during the data collection (47 h). The intensities were corrected for Lp but not for absorption. The structure was solved with standard Patterson and Fourier methods (SHELXS-86)[15] and refined on $F$ with SHELX-76.[16] All non-H atoms were refined with anisotropic thermal parameters. H atoms were located from a difference Fourier map and their positions refined with one common isotropic thermal parameter ($U_{iso}$ = 0.016 (2) Å$^2$). Final atomic coordinates are listed in Table II. Neutral scattering factors were obtained from ref 17 and corrected for anomalous dispersion.[18] The program PLATON[19] was used for geometrical calculations and for the preparation of the thermal motion ellipsoid plot. All calculations were carried out on a MicroVax cluster.

**Structure Determination of 11.** X-ray data were collected on an Enraf-Nonius CAD4-F diffractometer (graphite-monochromated Mo K$\alpha$ radiation) from a yellowish transparent crystal sealed in a Lindemann glass capillary. Unit cell parameters were obtained from SET4 setting angles[20] for 25 reflections in the range 9 < $\theta$ < 16°. Observed systematic absences are consistent with the space groups $Pca2_1$ and $Pcam$. The first one was adopted in this structure determination. Two reference reflections showed no decay during the 39 h of X-ray exposure time. The intensity data were corrected for Lp but not for absorption. The structure was solved with Patterson and Fourier methods (SHELXS-86)[15] and refined on $F$ by full-matrix least-squares treatment (SHELX-76).[16] Refinement with anisotropic thermal parameters for the non-hydrogen atoms revealed high thermal motion, in particular for the two cyclopentadienyl rings, with corresponding poor geometry. The two Cp rings were included in subsequent refinement as rigid groups with idealized geometry but individual anisotropic thermal parameters. Hydrogen atoms were introduced at calculated positions (C–H = 0.98 Å) and refined with two common isotropic thermal parameters. Scattering factors were obtained from ref 17 and corrected for anomalous dispersion.[18] Refinement of the structure with an opposite polarity did not result in lower $R$ values. The highest residual features in a final difference Fourier map can be interpreted as absorption artifacts or disorder peaks in the Cp-ring plane. The calculation of the geometrical data and the preparation of the thermal motion ellipsoid plot were performed with the program PLATON of the EUCLID package.[19] Crystal data and numerical details of the structure determination are given in Table I; positional parameters for the non-hydrogen atoms are listed in Table III.

**Structure Determination of 12.** X-ray data were collected on an Enraf-Nonius CAD4-F diffractometer (Zr-filtered Mo K$\alpha$ radiation) for a dark red block-shaped crystal sealed in a Lindemann glass capillary. Unit cell parameters were determined

(15) Sheldrick, G. M. SHELXS-86, Program for Crystal Structure Determination; University of Göttingen: Göttingen, FRG, 1986.
(16) Sheldrick, G. M. SHELX-76, Crystal Structure Analysis Package; University of Cambridge: England, England, 1976.
(17) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1967**, *A23*, 321.
(18) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.
(19) Spek, A. L. The EUCLID Package. In *Computational Crystallography*; Sayre, D., Ed.; Clarendon Press: Oxford, England, 1982; p 528.
(20) de Boer, J. L.; Duisenberg, A. J. M. *Acta Crystallogr.* **1984**, *A40*, C410.

## Table I. Crystal Data and Structural Analysis Results

| | 6 | 11 | 12 |
|---|---|---|---|
| formula | $C_{32}H_{28}Zr_2S_2$ | $C_{24}H_{30}Zr_2$ | $C_{20}H_{18}Zr_2S_2$ |
| fw | 659.13 | 500.94 | 504.92 |
| cryst syst | monoclinic | orthorhombic | orthorhombic |
| space group | $P2_1/n$ (No. 14) | $Pca2_1$ (No. 29) | $Fdd2$ (No. 43) |
| Z | 4 | 4 | 8 |
| $a$, Å | 9.929 (1) | 14.694 (1) | 22.523 (2) |
| $b$, Å | 16.017 (1) | 11.381 (1) | 20.446 (2) |
| $c$, Å | 16.641 (1) | 13.026 (2) | 8.001 (1) |
| $\beta$, deg | 97.67 (1) | | |
| $V$, Å$^3$ | 2622.8 (4) | 2178 (4) | 3684.3 (7) |
| $D_{calcd}$, g cm$^{-3}$ | 1.669 | 1.527 | 1.820 |
| $\mu$, cm$^{-1}$ | 9.5 | 9.5 | 13.3 |
| $F(000)$ | 1328 | 1016 | 2000 |
| cryst size, mm | 0.25 × 0.25 × 0.37 | 0.12 × 0.12 × 0.37 | 0.55 × 0.55 × 0.32 |
| $T$, K | 100 | 295 | 294 |
| radiation, $\lambda$, Å | Mo Kα (Zr), 0.710 73 | Mo Kα (Mon), 0.710 73 | Mo Kα (Zr), 0.710 73 |
| scan, deg | 0.60 + 0.35 tan θ | 0.90 + 0.35 tan θ | 0.60 + 0.35 tan θ |
| $\theta_{max}$, deg | 27.5 | 26.0 | 29.4 |
| range of $hkl$ | −12 to 0, 0 to 20, −21 to 21 | 0 to 18, 0 to 14, 0 to 16 | −30 to 30, −28 to 28, 0 to 11 |
| no. of rflns | 6440 | 2439 | 5279 |
| no. of unique rflns | 6009 | 2228 | 1351 |
| no. of rflns used | 4524 | 1528 | 1335 |
| no. of params | 410 | 218 | 111 |
| no. of rflns | 4524 | 1522 | 1335 |
| $R_F$ | 0.031 | 0.058 | 0.023 |
| $R_w$ | 0.031 | 0.064 | 0.025 |
| GOF | 1.76 | 2.70 | 2.78 |
| weighting scheme $w^{-1}$ | $\sigma^2(F)$ | $\sigma^2(F) + 0.0003F^2$ | $\sigma^2(F)$ |
| largest shift/esd | 0.2 | 0.2 | 0.17 |
| min, max resid dens, e Å$^{-3}$ | −0.59, 0.50 | −1.41, 0.98 | −0.97, 0.33 |

## Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 6

| atom | $x$ | $y$ | $z$ | $U(eq),^a$ Å$^2$ |
|---|---|---|---|---|
| Zr1 | 0.39206 (3) | 0.56298 (2) | 0.25281 (2) | 0.0123 (1) |
| Zr2 | 0.66268 (3) | 0.44266 (2) | 0.21759 (2) | 0.0123 (1) |
| S1 | 0.43220 (8) | 0.46823 (5) | 0.13568 (4) | 0.0140 (2) |
| S2 | 0.64762 (8) | 0.58264 (5) | 0.28787 (5) | 0.0142 (2) |
| C1 | 0.4193 (3) | 0.4353 (2) | 0.3383 (2) | 0.0146 (8) |
| C2 | 0.4223 (3) | 0.5044 (2) | 0.3923 (2) | 0.0177 (9) |
| C3 | 0.2937 (3) | 0.5424 (2) | 0.3817 (2) | 0.019 (1) |
| C4 | 0.2099 (3) | 0.4981 (2) | 0.3220 (2) | 0.020 (1) |
| C5 | 0.2854 (3) | 0.4326 (2) | 0.2939 (2) | 0.0166 (9) |
| C6 | 0.5349 (3) | 0.3851 (2) | 0.3234 (2) | 0.0140 (9) |
| C7 | 0.6722 (3) | 0.3956 (2) | 0.3603 (2) | 0.0167 (9) |
| C8 | 0.7544 (3) | 0.3391 (2) | 0.3235 (2) | 0.021 (1) |
| C9 | 0.6709 (3) | 0.2938 (2) | 0.2642 (2) | 0.020 (1) |
| C10 | 0.5363 (3) | 0.3213 (2) | 0.2631 (2) | 0.019 (1) |
| C11 | 0.4062 (4) | 0.6781 (2) | 0.1538 (2) | 0.031 (1) |
| C12 | 0.4188 (4) | 0.7173 (2) | 0.2296 (2) | 0.025 (1) |
| C13 | 0.2975 (4) | 0.7086 (2) | 0.2620 (2) | 0.023 (1) |
| C14 | 0.2055 (4) | 0.6651 (2) | 0.2043 (2) | 0.024 (1) |
| C15 | 0.2735 (3) | 0.6470 (2) | 0.1373 (2) | 0.029 (1) |
| C16 | 0.7594 (3) | 0.5255 (2) | 0.1104 (2) | 0.024 (1) |
| C17 | 0.7245 (4) | 0.4482 (3) | 0.0755 (2) | 0.029 (1) |
| C18 | 0.8065 (4) | 0.3878 (2) | 0.1174 (2) | 0.028 (1) |
| C19 | 0.8960 (3) | 0.4278 (2) | 0.1781 (2) | 0.024 (1) |
| C20 | 0.8674 (3) | 0.5136 (2) | 0.1737 (2) | 0.021 (1) |
| C21 | 0.3235 (3) | 0.3882 (2) | 0.0898 (2) | 0.0150 (9) |
| C22 | 0.3789 (3) | 0.3175 (2) | 0.0586 (2) | 0.0176 (9) |
| C23 | 0.2961 (4) | 0.2599 (2) | 0.0139 (2) | 0.021 (1) |
| C24 | 0.1573 (4) | 0.2716 (2) | 0.0003 (2) | 0.022 (1) |
| C25 | 0.1013 (3) | 0.3408 (2) | 0.0326 (2) | 0.021 (1) |
| C26 | 0.1833 (3) | 0.3989 (2) | 0.0774 (2) | 0.017 (1) |
| C27 | 0.7307 (3) | 0.6059 (2) | 0.3869 (2) | 0.0158 (9) |
| C28 | 0.8625 (3) | 0.5791 (2) | 0.4111 (2) | 0.020 (1) |
| C29 | 0.9285 (3) | 0.6002 (2) | 0.4872 (2) | 0.024 (1) |
| C30 | 0.8637 (4) | 0.6474 (2) | 0.5393 (2) | 0.026 (1) |
| C31 | 0.7327 (4) | 0.6746 (2) | 0.5155 (2) | 0.025 (1) |
| C32 | 0.6661 (3) | 0.6551 (2) | 0.4396 (2) | 0.019 (1) |

$^a$ $U(eq)$ is equal to one-third of the trace of the orthogonalized U matrix.

## Table III. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 11

| atom | $x$ | $y$ | $z$ | $U(eq),^a$ Å$^2$ |
|---|---|---|---|---|
| Zr1 | 0.1808 (1) | 0.5042 (2) | 0.1609 | 0.0383 (6) |
| Zr2 | 0.0750 (1) | 0.9825 (1) | 0.0000 (2) | 0.0352 (5) |
| C1 | 0.127 (1) | 0.717 (1) | 0.136 (2) | 0.043 (7) |
| C2 | 0.052 (1) | 0.661 (1) | 0.180 (2) | 0.042 (7) |
| C3 | 0.083 (2) | 0.626 (1) | 0.280 (2) | 0.062 (9) |
| C4 | 0.169 (2) | 0.660 (2) | 0.299 (2) | 0.065 (9) |
| C5 | 0.198 (1) | 0.717 (1) | 0.203 (2) | 0.045 (7) |
| C6 | 0.126 (1) | 0.767 (2) | 0.033 (2) | 0.031 (6) |
| C7 | 0.197 (1) | 0.831 (1) | −0.024 (2) | 0.052 (8) |
| C8 | 0.173 (2) | 0.862 (2) | −0.120 (3) | 0.07 (1) |
| C9 | 0.080 (2) | 0.821 (1) | −0.127 (2) | 0.060 (8) |
| C10 | 0.049 (2) | 0.764 (1) | −0.040 (2) | 0.060 (8) |
| C11 | 0.304 (1) | 0.440 (3) | 0.043 (2) | 0.12 (2) |
| C12 | 0.339 (1) | 0.538 (3) | 0.099 (2) | 0.10 (2) |
| C13 | 0.345 (1) | 0.505 (3) | 0.204 (2) | 0.08 (1) |
| C14 | 0.313 (1) | 0.388 (3) | 0.213 (2) | 0.12 (2) |
| C15 | 0.288 (1) | 0.348 (3) | 0.114 (2) | 0.12 (2) |
| C16 | −0.060 (1) | 1.051 (2) | 0.112 (2) | 0.10 (1) |
| C17 | −0.088 (1) | 0.952 (2) | 0.054 (2) | 0.13 (2) |
| C18 | −0.090 (1) | 0.984 (2) | −0.051 (2) | 0.10 (2) |
| C19 | −0.063 (1) | 1.103 (2) | −0.058 (2) | 0.08 (1) |
| C20 | −0.044 (1) | 1.145 (2) | 0.042 (2) | 0.12 (2) |
| C21 | 0.152 (1) | 1.014 (1) | 0.146 (2) | 0.056 (7) |
| C22 | 0.145 (2) | 1.126 (2) | −0.094 (2) | 0.09 (1) |
| C23 | 0.109 (2) | 0.474 (2) | 0.007 (2) | 0.090 (9) |
| C24 | 0.104 (1) | 0.368 (1) | 0.255 (3) | 0.063 (8) |

$^a$ $U(eq)$ is equal to one-third of the trace of the orthogonalized U matrix.

corrected for Lp, for a linear decay of 7.9% during the 96 h of X-ray exposure time, and for absorption (DIFABS)[22] and were averaged into a unique data set ($R_{av}$ = 2.7%). The structure was solved with standard Patterson and Fourier methods (SHELXS-86)[15] and refined on $F$ with SHELX-76.[16] Hydrogen atoms were introduced at calculated positions (C–H = 0.98 Å) and included in the final refinement riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen

from a least-squares treatment of the SET4 setting angles of 25 reflections with 10.4 < θ < 17.8°. The unit cell parameters were checked for the presence of higher lattice symmetry.[21] Data were

(21) Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578.
(22) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

## Table IV. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 12

| atom | $x$ | $y$ | $z$ | $U(eq)$,[a] $Å^2$ |
|------|-----|-----|-----|----------|
| Zr | 0.25735 (1) | 0.16687 (1) | 0.25 (-) | 0.0228 (1) |
| S | 0.17369 (4) | 0.24160 (4) | 0.1815 (2) | 0.0288 (3) |
| C1 | 0.2519 (2) | 0.2143 (2) | 0.5441 (5) | 0.031 (1) |
| C2 | 0.3048 (2) | 0.1764 (2) | 0.5352 (5) | 0.035 (1) |
| C3 | 0.2897 (2) | 0.1111 (2) | 0.5150 (7) | 0.041 (2) |
| C4 | 0.2268 (2) | 0.1066 (2) | 0.5102 (8) | 0.042 (1) |
| C5 | 0.2038 (2) | 0.1707 (2) | 0.5288 (6) | 0.037 (1) |
| C6 | 0.3071 (3) | 0.1202 (3) | −0.004 (1) | 0.068 (2) |
| C7 | 0.3107 (3) | 0.0731 (3) | 0.1147 (9) | 0.075 (3) |
| C8 | 0.2542 (4) | 0.0512 (2) | 0.1470 (8) | 0.079 (3) |
| C9 | 0.2167 (2) | 0.0868 (4) | 0.044 (1) | 0.075 (3) |
| C10 | 0.2500 (3) | 0.1289 (3) | −0.0475 (7) | 0.066 (3) |

[a] $U(eq)$ is equal to one-third of the trace of the orthogonalized U matrix.

### Scheme I
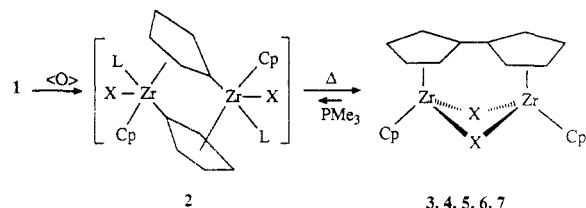
$$<O> = R_3PX_2 \; [R=n\text{-}Bu,Me; \; X=Cl(3),Br(4),I(2a)(5); \; L=PMe_3(2a)], \; PhSSPh[X= SPh(2b)(6)]; \; Me_2PPMe_2[X=PMe_2(7)]$$

atoms were refined with two separate common isotropic thermal parameters. The crystal exhibited some secondary extinction, for which the $F_c$ values were corrected by refining an empirical isotropic extinction parameter $(X = 1.7 \; (1) \times 10^{-8}; \; F_c' = F_c[1 - (XF^2/\sin\theta)])$. Weights were introduced in the final refinement cycles; convergence was reached at $R = 0.023$ and $R_w = 0.025$. Refinement of the structure with an opposite anomalous dispersion did not result in lower $R$ values. Scattering factors were obtained from ref 17 and corrected for anomalous dispersion.[18] Crystal data and numerical details of the structure determination are given in Table I; positional parameters for the non-hydrogen atoms are listed in Table IV.

## Results and Discussion

As described in Scheme I, the oxidation of [CpZr-(PMe₃)($\eta^1$:$\eta^5$-C₅H₄)]₂ (1) to fulvalene–Zr(III) complexes may be carried out with several different reagents. While the direct oxidation with $X_2$, $CX_4$ and $CHX_3$ (X = Cl, Br) led to the formation of CpZrX₃, milder agents allowed the initial formation of intermediate Zr(IV) species [CpZrX-(L)($\eta^1$:$\eta^5$-C₅H₄)]₂ (2), in which the fulvalene ligand had not yet been formed. These thermally unstable intermediates are essentially the same as those involved in the controlled oxidation of Zr(II) complexes[10b] and cannot be isolated under ordinary reaction conditions.

In most cases, the oxidation reaction led directly to the formation of the fulvalene systems, and the isolation of the intermediates 2 in analytically pure form was possible only in the cases of 2a (X = I, L = PMe₃) and 2b (X = SPh). The reductive elimination of 2b during the formation of 6 occurs rapidly in boiling THF and instantaneously in pyridine at room temperature. Conversely, the transformation of the phosphine-containing 2a into the fulvalene Zr(III) iodide 5 is reversible and can be achieved quantitatively only when PMe₃ is distilled out from a suspension of 2a in boiling toluene. The equilibrium can be quantitatively reversed to 2a simply by treatment of 5 with a small excess of phosphine in toluene at room temperature. Although there is no evidence for such a reversibility in any of the other cases, its occurrence is quite baffling and
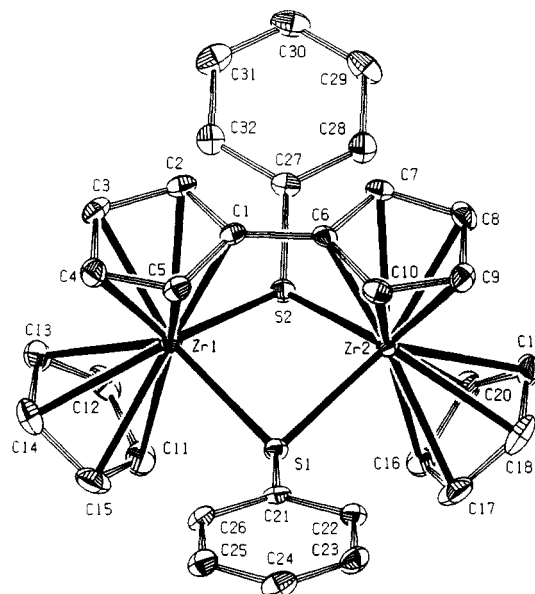
**Figure 1.** Thermal motion ellipsoid plot (50% probability) for 6 with the labeling scheme.

### Scheme II
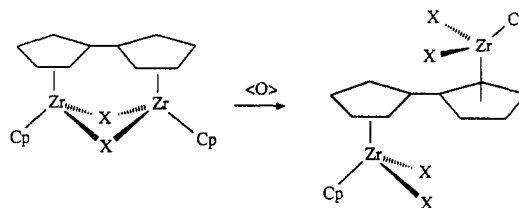
indicates fulvalene cleavage as a possible reaction pathway. In all cases, the reaction sequence reported in Scheme I allowed the convenient preparation of Zr(III) complexes [$\eta^5$:$\eta^5$-C₁₀H₈][CpZrX]₂ (X = Cl (3), Br (4), I (5), SPh (6), PMe₂ (7)) in crystalline form.

The NMR spectra of all the fulvalene complexes 3–7 are consistent with the structure proposed in Scheme I, as also demonstrated by X-ray analysis in the cases of 3[1b] and 5.[10f] The fulvalene ligand causes two characteristic pseudo-triplets to appear in the ¹H NMR spectrum at higher field with respect to the singlet of the cyclopentadienyl rings. The bridgehead carbon atom could not always be located in the ¹³C NMR spectra.

The controversy over the formation of Zr–Zr bonds,[10f] and our long-term goal of understanding the role of the bridging donor atom in determining both the value of the intermetallic separation and the nature of the Zr···Zr interaction in these diamagnetic Zr(III) complexes, prompted us to undertake a further X-ray structure determination of complex 6. The crystal consists of discrete molecules of [$\eta^5$:$\eta^5$-C₁₀H₈][CpZrSPh]₂ (Figure 1), isostructural with 3[1b] and 5.[10f] However, the folding of the Zr₂(SPh)₂ core along the Zr–Zr vector is more pronounced in this case (S1–Zr1–Zr2–S2 = 145.47 (4)°). The geometry around each sulfur atom is pyramidal, with the phenyl ring bent toward the fulvalene ligand. In analogy to the case for 5,[10f] there is no Zr–Zr bond in the diamagnetic 6 (Zr1···Zr2 = 3.420 (1) Å). The Zr···Zr distance compares well with that found in 5 and, due to the almost perfect planarity of the fulvalene ligand (C2–C1–C6–C7 = 0.3 (5)°, C2–C1–C6–C10 = −172.7 (3)°), is close to the optimal metal–metal distance expected for a cis-fulvalene bimetallic complex.[23]

(23) The calculated M–M optimal distance for fulvalene complexes is 4.0 Å: Smart, J. C.; Curtis, C. J. *J. Am. Chem. Soc.* **1977**, *99*, 3518.

**Table V. Selected Bond Distances (Å) and Angles (deg)**

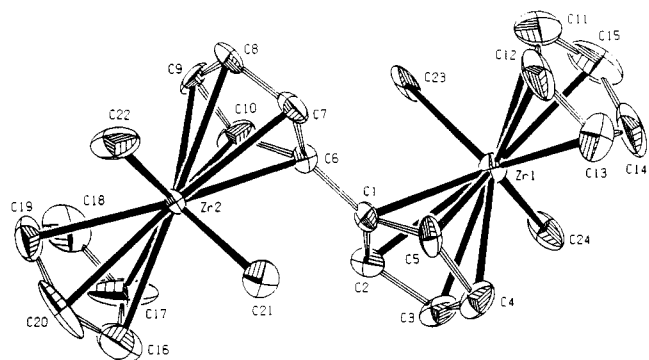| 6 | | 11 | | 12 | |
|---|---|---|---|---|---|
| Zr1-S1 | 2.533 (1) | Zr1-C24 | 2.28 (3) | Zr-S | 2.487 (1) |
| Zr2-S2 | 2.546 (1) | Zr1-C23 | 2.29 (3) | Zr-S′ | 2.493 (1) |
| Zr1-S1-Zr2 | 84.66 (3) | C24-Zr1-C23 | 98.1 (1) | S-Zr-S′ | 87.85 (1) |
| S1-Zr1-S2 | 89.78 (3) | C5-C1-C6-C10 | 178.5 (1) | Zr-S-Zr′ | 86.60 (3) |
| Zr1-S1-Zr2-S2 | 24.84 (3) | C2-C1-C6-C7 | 178.2 (2) | C2-C1-C1′-C5′ | 2.6 (7) |
| S1-Zr1-Zr2-S2 | 145.47 (3) | | | C2-C1-C1′-C2′ | 172.9 (4) |
| C2-C1-C6-C7 | 0.3 (5) | | | S-Zr-Zr′-S′ | -144.81 (5) |
| C2-C1-C6-C10 | -172.7 (3) | | | | |



**Figure 2.** Thermal motion ellipsoid plot (30% probability) for 11 with the labeling scheme.

Further oxidation of 3-6 to Zr(IV) fulvalene complexes could be achieved during fast reactions upon treatment with an excess of oxidizing agent (Scheme II). The very poor solubility of the tetrahalide fulvalene derivatives in most common solvents facilitated their high-yield isolation. The tetrathiophenolate derivative $[\eta^5:\eta^5\text{-}C_{10}H_8][CpZr(SPh)_2]_2$ (10) was prepared in crystalline form. Reproducible analytical data consistent with the proposed formulation were obtained in all cases. The $^1$H NMR data showed the usual symmetric pattern with the multiplets attributable to the fulvalene ligand considerably shifted to low field. This might suggest that a significant modification of the structure had occurred with respect to the cis configuration of the $[\eta^5:\eta^5\text{-}C_{10}H_8][CpZrX]_2$ derivatives. A crystal of $[\eta^5:\eta^5\text{-}C_{10}H_8][CpZr(CH_3)_2]_2$ (11) suitable for X-ray analysis was prepared by extensive methylation of 8 or 10 with 4 equiv of MeLi.[24]

The structure as solved by X-ray analysis is shown in Figure 2. Apart from the trans dinuclear disposition, the geometry around each zirconium atom closely resembles that for the mononuclear Cp₂ZrMe₂, with comparable bond distances and angles.[25]

The chemistry of the zirconium–carbon bond is very rich, and many attractive features have been reported.[26] For this reason, complex 11 is a promising substrate with which to verify the hypothesis that a concerted or cooperative interaction of the two metal centers with a substrate might lead to transformations which do not occur with mononuclear systems. A prerequisite for this is the presence in complex 11 of a high degree of rotational freedom around the C-C linkage of the fulvalene ligand, which is able to restore the cis configuration of the two

(24) The $^1$H NMR data are consistent with the structure as obtained by the X-ray analysis and are slightly in disagreement with those of a previous literature report: (a) Herrmann, W. A.; Cuenca, T.; Menjon, B.; Herdtweck, E. *Angew. Chem., Int. Ed. Engl.* **1987**, 26, 687. (b) Cuenca, T.; Hermann, W. A.; Ashworth, T. V. *Organometallics* **1986**, 5, 2514.

(25) Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Pentilla, R. E.; Atwood, J. L. *Organometallics* **1983**, 2, 750.

(26) For a comprehensive review of the chemistry of the zirconium-carbon bond see: Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organozirconium and -hafnium Compounds*; Ellis Horwood: Chichester, England, 1986.
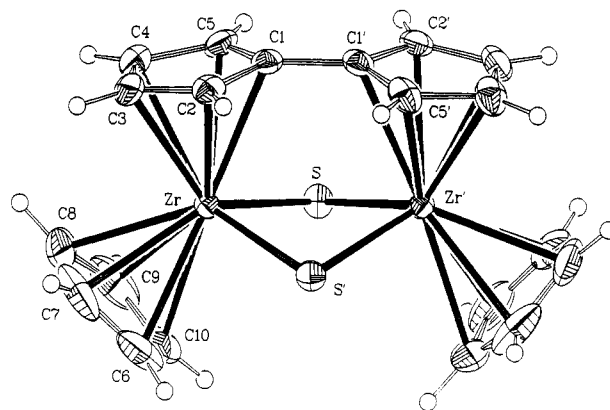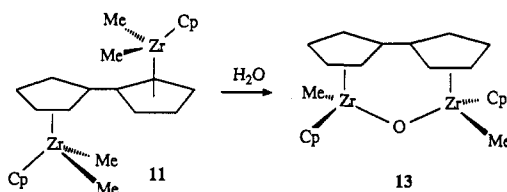
**Scheme III**
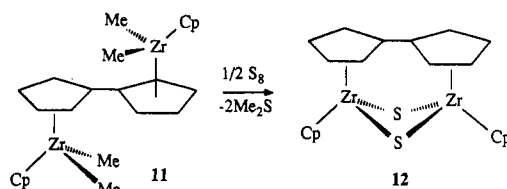


**Scheme IV**





**Figure 3.** Thermal motion ellipsoid plot (40% probability) for 12 with the labeling scheme.

metal centers. This has been tested in two cases by reacting complex 11 with S₈ and H₂O.

A fast reaction took place between 11 and S₈ in toluene (Scheme III) with elimination of Me₂S and formation of the bright red $[\eta^5:\eta^5\text{-}C_{10}H_8][CpZrS]_2$ (12). However, all attempts to arrest the putative reaction intermediate $[\eta^5:\eta^5\text{-}C_{10}H_8][CpZrMe]_2[\mu\text{-}S]$, by carefully controlling the stoichiometry and the reaction conditions, failed. Complex 12 can be synthesized more conveniently by direct reaction of 1 or 6 with sulfur in toluene. The cis arrangement is suggested by the characteristic shape and the δ values of the multiplets in the $^1$H NMR spectrum attributable to the fulvalene and has been confirmed by X-ray analysis. As expected, 12 is isostructural with the trivalent zirconium congeners, the overall geometry being shown in Figure 3. The geometry of the Zr₂S₂ core (Table V) appears to be almost identical with that observed in the closely related $[Cp_2ZrS]_2$.[27] The most significant difference is the de-

(27) Bottomley, F.; Drummond, D. F.; Eghorevba, G. O.; White, P. S. *Organometallics* **1986**, 5, 1620.

**Scheme V**



$11 + 2CO \rightleftharpoons$

14
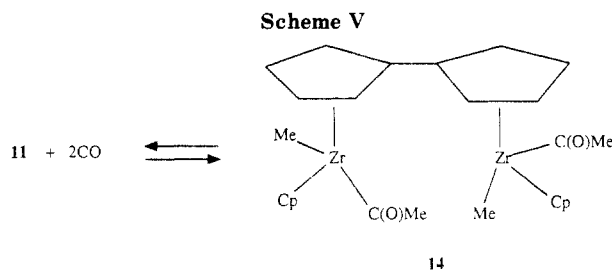
viation from planarity, which is probably a consequence of the shorter Zr···Zr distance (3.4154 (5) against 3.529 (2) Å) caused by the fulvalene ligand.

This species is quite stable, and any attempt to functionalize it by replacing one bridging sulfide with two methyl groups led only to mixtures of 11 and unreacted 12. Conversely, two reactive methyl groups were preserved in the molecular frame during the formation of the cis $\mu$-oxo species $[\eta^5:\eta^5\text{-}C_{10}H_8][CpZrCH_3]_2[\mu\text{-}O]$ (13) in a more controllable reaction of 11 with stoichiometric amounts of $H_2O$ (Scheme IV). The close similarity of the fulvalene pattern in the $^1H$ NMR spectrum of 13 with that of $[\eta^5:\eta^5\text{-}C_{10}H_8][CpZrCl]_2[\mu\text{-}O]^{11a}$ indicates that the two complexes are probably isostructural.

Having demonstrated the free or at least easy rotation of the two rings around the C–C linkage and the ability of bridging ancillary ligands to constrain the two reactive centers to the same side of the molecule, we have made a preliminary probe into the reactivity of complex 11 with CO. The choice of CO as a substrate has been dictated by the strong interest roused in the literature, from the reactivity of the transition-metal–acyl compounds.[26,29,30] In general, the result of the insertion of CO into a Zr–C bond depends on the presence of substituents on the Cp rings, and there is no indication that the reaction can take place through a cooperative interaction of two or more metal centers with the substrate. While a reversible insertion into one of the two Zr–C bonds has been observed for $Cp_2ZrMe_2$,[29] the permethylated congener $Cp^*_2ZrMe_2$ allows a slow second insertion (70 °C) with final formation

of a mononuclear metallacyclic system.[30] According to Scheme V, the reversible reaction of 11 with 2 equiv of CO takes place rapidly at room temperature, forming the bis(acyl) complex 14.

The presence of two very intense resonances centered at 318 ppm in the $^{13}C$ NMR spectrum of the $^{13}CO$-enriched complex suggested the presence of two inequivalent acetyl groups. This was confirmed by the splitting of the NMR resonances ($^1H$, $^{13}C$) of both the acylic and alkylic methyls (doublets in the $^{13}CO$-enriched spectrum) and by the presence in the IR spectrum of two intense absorptions attributable to the $\nu_{CO}$ stretching modes (1540 and 1130 cm$^{-1}$) of the two inequivalent acetyls. An asymmetric pattern has also been observed for fulvalene in both the $^1H$ and $^{13}C$ NMR spectra.

The presence of two acetyl groups with different degrees of hapticity provides a possible rationalization of these experimental results. We cannot, however, exclude other alternative explanations, such as the formation of diastereoisomeric mixtures of *R,R*, *S,S*, and *R,S* trans-bis(acyl) derivatives, which might equally well account for the observed spectroscopic features.

In conclusion, the present results do not corroborate our early contention that dinuclear zirconium fulvalene systems can modify the reactivity through a cooperative interaction of the twinned metals on the substrate; however, they do show that such interaction is possible and encourage further work to test the possible utilization of these systems.

**Registry No.** 1, 107633-86-3; **2a**, 127516-96-5; **2b**, 127492-30-2; 3, 100946-29-0; 4, 127492-25-5; 5, 75880-97-6; 6, 127492-26-6; 7, 127492-27-7; 8, 108947-07-5; 9, 127516-93-2; 10, 127516-94-3; 11, 108947-09-7; 12, 127492-28-8; 13, 127516-95-4; 14, 127492-29-9; $Bu_3PCl_2$, 17417-07-1; $Bu_3PBr_2$, 4092-19-7; $Bu_3PI_2$, 21473-75-6; PhSSPh, 882-33-7; $Me_2PPMe_2$, 3676-91-3.

**Supplementary Material Available:** Tables of thermal parameters, H atom positional parameters, and bond angles and distances for 6, 11 and 12 and a table of selected torsion angles for 12 (18 pages); lists of observed and calculated structure factors (60 pages). Ordering information is given on any current masthead page.

(28) See for example: (a) Rusik, C. A.; Collins, M. A.; Gamble, A. S.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 2550. (b) Casey, C. P.; Nagashima, H. *J. Am. Chem. Soc.* **1989**, *111*, 2352. (c) Waymouth, R. M.; Santarsiero, B. D.; Cools, R. J.; Bronikowski, M. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 1427. (d) Martin, B. D.; Matchett, S. A.; Norton, J. R.; Anderson, O. P. *J. Am. Chem. Soc.* **1985**, *107*, 7952. (e) Cutler, A.; Raja, M.; Todora, A. *Inorg. Chem.* **1987**, *26*, 2877.

(29) Fachinetti, G.; Floriani, C.; Marchetti, M.; Merlino, S. *J. Chem. Soc., Chem. Commun.* **1976**, 522.

(30) (a) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. (b) Hoffmann, P.; Frede, M.; Stauffert, P.; Lasser, W.; Thewalt, U. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 712.