Preparation of Dinuclear Zirconium Hydride Complexes Containing the Fulvalene Ligand and Their Reactions with Carbon Monoxide

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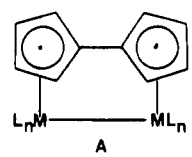
The isolation of the lithium salt of the fulvalene dianion $Li_2(C_{10}H_8)$ is reported. Metathesis of this dianion with 2 equiv of $(Cp^*ZrCl_3)_x$ ($Cp^* = \eta^5$-C_5Me_5) yields the dinuclear zirconium complex $(C_{10}H_8)[Cp^*ZrCl_2]_2$ (1). Treatment of 1 with 4 equiv of CH_3Li yields the tetramethyl complex $(C_{10}H_8)[Cp^*Zr(CH_3)_2]_2$ (2). The reaction of 2 with H_2 produces the tetrahydride complex $(C_{10}H_8)[Cp^*ZrH_2]_2$ (3). Complex 3 reacts selectively with $CHCl_3$ to yield the hydrido chloride complex $(C_{10}H_8)[Cp^*Zr(H)Cl]_2$ (4). Complexes 3 and 4 react with CO under mild conditions to yield products containing bridging formaldehyde ligands, $(C_{10}H_8)[Cp^*Zr(OCH_2)]_2$ (7) and $(C_{10}H_8)[Cp^*ZrCl]_2(OCH_2)$ (6), respectively. Complexes 3 and 6 are fluxional on the nuclear magnetic resonance (NMR) time scale and the dynamic processes were studied by variable-temperature ^1H NMR. The structure of 7 was determined by X-ray diffraction. Complex 7 crystallizes in a monoclinic unit cell with $P2_1$ symmetry with a = 8.273 (2) Å, b = 15.383 (4) Å, c = 11.250 (3) Å, β = 101.26 (2)°, V = 1404.1 (7) Å^3, Z = 2, and d_{calcd} = 1.516 g/cm^3. Full-matrix least-squares refinement converged with final residuals R = 5.10% and R_w = 5.80%.

Introduction

The chemistry of dinuclear organometallic complexes containing the fulvalene ligand has recently become a topic of renewed interest.[1–4] The fulvalene ligand is flexible and can accommodate structures with metal–metal bonds (A),[1,14] additional bridging ligands,[5] and open trans geometries (B), providing complexes with a range of metal–metal distances and different degrees of electronic communication between the metals. Such complexes have been studied as models for the interaction of organic fragments with metal surfaces and as potential catalysts for synthetic organic transformations. Fulvalene complexes also offer the opportunity to compare the properties of analogous mono- and dinuclear complexes in order to test the hypothesis that cooperative interaction of two metal centers with a substrate can lead to transformations that do not occur when only one metal is present.



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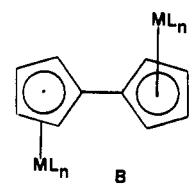

B

Three general methods for the preparation of transition-metal fulvalene complexes have been employed. The first route involves coupling of cyclopentadienyl ligands in metal cyclopentadienyl complexes. An example of this type of coupling was discovered serendipitously when attempts to synthesize titanocene by reduction of bis(cyclopentadienyl)titanium(IV) species yielded a fulvalene complex.[5,6] Reductive coupling of cyclopentadienyl ligands has now been observed for complexes of Zr,[3,4,7] Nb,[8] and Mo[9] also. Oxidative coupling of a mononuclear rhodium complex to generate a fulvalene dirhodium complex has also been demonstrated.[10] Designed syntheses of metallofulvalene complexes have used Ullmann coupling of halocyclopentadienyl complexes to produce complexes such as $(\eta^5{:}\eta^5$-$C_{10}H_8)Cp_2Fe_2$ ($Cp = \eta^5$-C_5H_5),[11] $(\eta^5{:}\eta^5$-$C_{10}H_8)_2Fe_2$,[12] $(\eta^5{:}\eta^5$-$C_{10}H_8)Mn_2(CO)_6$,[12b] and $(\eta^5{:}\eta^5$-$C_{10}H_8)Cp_2Ru_2$.[13] However, the generality of this method is limited by the availability of suitable halocyclopentadienyl starting materials.

The second and most recently developed route to metallofulvalene complexes involves the reaction of di-

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hydrofulvalene with metal carbonyls to yield fulvalene dimetal carbonyl complexes. This route has been employed to synthesize $(\eta^5:\eta^5\text{-}C_{10}H_8)(CO)_4Co_2$, $(\eta^5:\eta^5\text{-}C_{10}H_8)(CO)_6M_2$ (M = Cr, Mo, W), and the mixed-metal complex $(\eta^5:\eta^5\text{-}C_{10}H_8)(CO)_5MoRu$.[14] A new synthetic strategy for the preparation of heterobimetallic fulvalene complexes and its use for the preparation of several heterobimetallic carbonyl complexes has been reported.[15]

The third method used to prepare metallofulvalene complexes involves nucleophilic substitution reactions of metal substrates with the fulvalene dianion. This method has been used to synthesize a number of bis(fulvalene) dimetal complexes[16] as well as a fulvalene metal carbonyl complex.[17] We report here the isolation of the lithium salt of the fulvalene dianion by deprotonation of dihydrofulvalene prepared free of alkali-metal halides by the procedure of Vollhardt and Weidman[14] and the use of this material to synthesize the dinuclear zirconium complex $(\eta^5:\eta^5\text{-}C_{10}H_8)[Cp^*ZrCl_2]_2$ (1, Cp* = $\eta^5\text{-}C_5Me_5$).

Fulvalene complexes of the group 4 transition metals had been confined, until recently, to compounds of titanium synthesized by reduction of bis(cyclopentadienyl)titanium(IV) complexes.[6] Similar chemistry was observed for zirconium,[7] but well-characterized examples of fulvalene zirconium complexes have been prepared only recently by reduction of Cp_2ZrCl_2[3,18] and by comproportionation of Cp_2ZrCl_2 and $Cp_2Zr(PMe_3)_2$.[2] Both of these reactions yield $(\eta^5:\eta^5\text{-}C_{10}H_8)[CpZr(\mu\text{-}Cl)]_2$, a fulvalene complex of Zr(III), which has been characterized by X-ray diffraction.[2] Some of the reaction chemistry of this complex has been explored.[4]

A more useful, high-yield preparation of fulvalene complexes of both Zr(III) and Zr(IV) has appeared recently.[19] It relies on oxidation of $[CpZr(PMe_3)(\eta^1:\eta^5\text{-}C_5H_4)]_2$ with mild oxidants such as R_3PX_2 (R = *n*-Bu, Me; X = Cl, Br, I), PhSSPh, Me_2PPMe_2, and S_8 to bring about coupling of the $(\eta^1:\eta^5\text{-}C_5H_4)$ ligands and generate Zr(III) complexes $(\eta^5:\eta^5\text{-}C_{10}H_8)(CpZrX)_2$ (X = Cl, Br, I, SPh, PMe_2) and Zr(IV) complexes $(\eta^5:\eta^5\text{-}C_{10}H_8)(CpZrX_2)_2$ (X = Cl, I) and $(\eta^5:\eta^5\text{-}C_{10}H_8)(CpZrS)_2$. The chloro Zr(IV) complex was converted to the corresponding methyl derivative by using methyllithium.

A number of early-transition-metal hydride complexes react stoichiometrically with carbon monoxide to give products in which CO has been reduced. Floriani and co-workers first reported that $[Cp_2Zr(H)(Cl)]_x$ reacts with carbon monoxide under mild conditions to yield $[Cp_2ZrCl]_2(\mu\text{-}CH_2O)$.[20] Subsequent characterization of this product by X-ray diffraction[21] and variable-temperature NMR[22] showed that the bridging (CH_2O) fragment is η^2-C,O bonded to one zirconium and O bonded to the other zirconium and undergoes a dynamic process with the carbon going back and forth between the two metals.

Bercaw and co-workers have examined the reduction of carbon monoxide with the monomeric hydrides $Cp^*_2MH_2$ (M = Zr,[23] Hf[24]). They observe reduction of CO to coordinated methoxide and reductive coupling to *cis*- and *trans*-enediolate and saturated glycolate ligands bridging two metal centers, depending on the conditions employed. Erker and co-workers examined the carbonylation reaction of $[Cp_2ZrH_2]_x$ and found that it yields the cyclic trimer $[Cp_2Zr(\mu\text{-}\eta^1:\eta^2\text{-}CH_2O)]_3$, which was characterized by X-ray diffraction.[25]

In group 5, Schrock and co-workers have prepared a dinuclear tantalum hydride $[(\eta^5\text{-}C_5Me_4Et)TaCl_2H]_2$[26] and shown that it reacts with CO to give $[(\eta^5\text{-}C_5Me_4Et)TaCl_2](\mu\text{-}H)(\mu\text{-}CHO)$,[27] which contains a doubly bridging formyl ligand.

We are interested in reactions of small molecules at two metal centers and in comparing the reactivity of dinuclear complexes with that observed for analogous mononuclear systems. We report here the preparation of 1, its conversion to tetramethyl, tetrahydride, and hydridochloride derivatives, the reactions of these hydrides with carbon monoxide, and the X-ray crystal structure of one of the carbon monoxide reduction products.

Experimental Section

General Considerations. Reagent grade tetrahydrofuran (THF) was predried over CaH_2. Toluene, THF, and hexane were purified by distillation from sodium–benzophenone ketyl and stored under argon. Heptane was deoxygenated by purging with argon just prior to use. Toluene-d_8 and CD_2Cl_2 were purified by vacuum transfer from CaH_2 and stored in an inert atmosphere glovebox. Dry chloroform free of stabilizers was obtained by shaking reagent grade chloroform with concentrated H_2SO_4 and then water and drying over $CaCl_2$, followed by distillation from P_2O_5 under argon.

$[Cp^*ZrCl_3]_x$[29] and $Na(DME)C_5H_5$[17] were prepared by published procedures. Methyllithium in diethyl ether and butyllithium in hexane were obtained from Aldrich. Ultrahigh-purity hydrogen gas was used without purification.

Air-sensitive solids were stored and manipulated in a helium-filled Vacuum Atmospheres glovebox equipped with a freezer. Reactions were carried out in dry, deoxygenated solvents using standard cannula and Schlenk techniques. Carbonylation reactions and Toepler pump experiments were carried out on a high-vacuum line. Carbon monoxide was passed over MnO on vermiculite and activated 4-Å molecular sieves.[28] Fischer-Porter bottles and attendant stainless steel fittings were obtained from Fisher & Porter Co., Lab-crest Scientific Division, Warminster, PA.

NMR spectra were obtained using a JEOL FX-90Q spectrometer operating at 89.55 MHz for ^1H and 22.50 MHz for ^{13}C or with a Varian Unity 300 spectrometer. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane. Infrared spectra were obtained on a Perkin-Elmer 599B spectrophotometer. Melting points were determined on a Thomas/Hoover apparatus using sealed capillary tubes for air-sensitive samples and are uncorrected. Microanalyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI, and Huffman Laboratories, Golden, CO.

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Isolation of $Li_2C_{10}H_8$. The procedure of Vollhardt and Weidman[14b] was used to prepare a heptane solution of dihydrofulvalene starting from $Na(DME)C_5H_5$ (10.76 g, 60.3 mmol) in THF (200 mL) in a 1-L flask. The following modifications were made to minimize polymerization of dihydrofulvalene and exposure to air. After the iodine coupling and the addition of cold heptane (300 mL) and cold aqueous 1% $Na_2S_2O_3$, the two-phase mixture was shaken and allowed to separate and then quickly cooled to −78 °C. This caused the aqueous layer to freeze and the heptane layer was then decanted via cannula into a cold (−78 °C), argon-filled, 1-L flask containing Na_2SO_4 (75 g). The orange solution was allowed to warm and stir with the drying agent for 15 min; then it was decanted via cannula into a cold (−78 °C), argon-filled, 1-L flask. To this was added *n*-butyllithium (25.0 mL of a 2.6 M solution in hexane, 65.0 mmol), causing the color to change to dark purple and then lighten as white solid precipitated. The suspension was warmed to room temperature and stirred for 2 h; then it was transferred via cannula to a Schlenk fritte capped with a septum. The white solid was collected by filtration, washed with hexane (2 × 50 mL), and dried under vacuum for 8 h to yield 4.1 g (96%) of product as a fine white powder. This material turns purple and then blue on exposure to small amounts of oxygen; it is pyrophoric in air. The equivalent weight, determined by adding degassed water and titrating the base produced with standard HCl, was 70.5 ± 0.5 g/equiv (theory 71.0).

(η^5:η^5-$C_{10}H_8$)[Cp*ZrCl$_2$]$_2$ (1). (Cp*ZrCl$_3$)$_x$ (18.63 g, 56.0 mmol) and $Li_2C_{10}H_8$ (4.00 g, 28.1 mmol) were combined in a 500-mL flask and toluene (300 mL) was added. The yellow suspension was stirred and heated at reflux for 3 days. The solvent was removed under vacuum to give a yellow powder. This was treated with CH_2Cl_2 (300 mL) and 4 M HCl (100 mL) in air, which caused the color to change to dark green. The green organic layer was separated and the aqueous layer was further extracted with CH_2Cl_2 (2 × 50 mL). The combined CH_2Cl_2 extract was then dried over $MgSO_4$ and filtered through a 1-in. bed of Celite, and the solvent was removed on a rotary evaporator. The resulting green solid was then placed in a fritted funnel and washed with portions of chlorobenzene until no green color remained (4 × 10 mL). The remaining yellow solid was then recrystallized from boiling chlorobenzene (300 mL) in air to yield 14.35 g (70%) of crystalline yellow product obtained in three crops. Mp 281 °C dec; ^{1}H NMR ($CDCl_3$) δ 6.53 (t, 4 H, *J* = 2.8 Hz), 5.98 (t, 4 H, *J* = 2.8 Hz), 2.01 (s, 30 H). Anal. Calcd for $C_{30}H_{38}Cl_4Zr_2$: C, 49.84; H, 5.30; Cl, 19.62. Found: C, 49.82; H, 5.36; Cl, 19.57.

(η^5:η^5-$C_{10}H_8$)[Cp*Zr(CH$_3$)$_2$]$_2$ (2). Tetrachloride complex 1 (1.45 g, 2.01 mmol) was placed in a 250-mL flask and toluene (125 mL) was added. The yellow suspension was then treated with CH_3Li solution (7.0 mL of a 1.3 M solution in diethyl ether, 9.1 mmol) and stirred for 3 h to give a colorless solution with white suspended solid. This was filtered and the white solid collected was washed with toluene (2 × 15 mL) and discarded. The volume of the combined filtrate was then reduced to 80 mL under vacuum, and then the solution was heated under Ar until all of the solid that had precipitated redissolved. Slow cooling to −25 °C produced clusters of colorless needles. These were isolated by decanting the solvent via cannula at −25 °C, washed with cold toluene (5 mL) and then hexane (10 mL), and dried under vacuum to yield 1.08 g (83%) of 2 in two crops. Mp 220 °C dec; ^{1}H NMR (toluene-d_8) δ 6.14 (t, 4 H, *J* = 2.6 Hz), 5.28 (t, 4 H, *J* = 2.6 Hz), 1.74 (s, 30 H), −0.39 (s, 6 H). Anal. Calcd for $C_{34}H_{50}Zr_2$: C 63.69; H, 7.86. Found: C, 63.45; H, 7.82.

(η^5:η^5-$C_{10}H_8$)[Cp*ZrH$_2$]$_2$ (3). In a dry, 3-oz Fischer-Porter bottle, tetramethyl complex 2 (1.02 g, 1.59 mmol) was combined with 25 mL of toluene to give a colorless suspension. The bottle was pressurized with H_2 (UHP) to 300 psi and placed in an oil bath at 80 °C. The solution was heated and stirred for 19 h, during which it darkened and white, microcrystalline solid precipitated. The mixture was cooled to room temperature and vented, and the slurry was transferred via cannula to a Schlenk fritte. The white solid was collected by filtration, washed with toluene (2 × 5 mL), and dried under vacuum to give 0.77 g (83%) of analytically pure product. Mp 239 °C dec; ^{1}H NMR (toluene-d_8, −52 °C) δ 6.43 (m, 2 H), 5.45 (m, 2 H), 5.05 (m, 2 H), 4.73 (m, 2 H), 4.02 (t, 2 H, *J* = 8.1 Hz, ZrH$_t$), 1.97 (s, 30 H), −1.68 (t, 2 H, *J* = 8.1 Hz, ZrH$_b$); IR (Nujol) $\nu_{Zr-H(D)}$ 1162 (1125), 1255 (902) cm^{-1}. Anal. Calcd for $C_{30}H_{42}Zr_2$: C, 61.58; H, 7.24. Found: C, 61.55; H, 7.25.

Table I. Crystal Data for ($C_{10}H_8$)[Cp*Zr(OCH$_2$)]$_2$ (7)

formula	$C_{32}H_{42}O_2Zr_2$	vol, Å^3	1404.1 (7)
fw	641.1	*Z*	2
space group	$P2_1$	d_{calcd}, g/cm^3	1.516
cryst system	monoclinic	*F*(000), e$^-$	660
a, Å	8.273 (2)	μ, cm^{-1}	7.56
b, Å	15.383 (4)	radiatn, Å	Mo Kα (λ = 0.71073)
c, Å	11.250 (3)	temp, °C	22–24
β, deg	101.26 (2)	*R*, R_w	0.0510, 0.0580

(η^5:η^5-$C_{10}H_8$)[Cp*Zr(H)Cl]$_2$ (4). A suspension of tetrahydride complex 3 (0.76 g, 1.30 mmol) in toluene (100 mL) was treated with $CHCl_3$ (0.25 mL, 0.37 g, 3.12 mmol) added dropwise from a syringe. The solution began to turn yellow immediately, and after 30 min a clear, yellow solution was present. Methylene chloride and chloroform were then removed under vacuum and the volume of the solution was reduced about 10 mL. It was then cooled slowly to −25 °C, and yellow needles precipitated. These were collected by filtration, washed with cold toluene (5 mL) and hexane (10 mL), and dried under vacuum to yield 0.73 g of 4 as the monotoluene solvate (75% yield). Mp 185 °C dec; ^{1}H NMR (toluene-d_8) δ 6.00 (m, 2 H), 5.75 (m, 2 H), 5.54 (m, 2 H), 4.96 (m, 2 H), 1.87 (s, 30 H), 0.95 (s, 2 H, ZrH); IR (Nujol) $\nu_{Zr-H(D)}$ 1360 (976) cm^{-1}. Anal. Calcd for $C_{30}H_{40}Cl_2Zr_2 \cdot C_7H_8$: C, 59.56; H, 6.48; Cl, 9.50. Found: C, 59.72; H, 6.54; Cl, 9.85, 9.72.

(η^5:η^5-$C_{10}H_8$)[Cp*ZrCl]$_2$ (5). In a flame-dried flask under argon, a suspension of 1 (0.89 g, 1.23 mmol) in THF (125 mL) was prepared. This was treated with Na(Hg) (10.69 g, 0.54% Na, 2.52 mmol) added via syringe. The mixture immediately turned dark green and was stirred for 2 h. The solution was then decanted from the mercury and filtered. THF was removed from the filtrate under vacuum, the green residue was dissolved in toluene (125 mL) at 60 °C, and the hot solution was filtered. The volume of the filtrate was reduced under vacuum at 60 °C to about 100 mL, and then it was cooled to −30 °C. The crystals that formed were collected, washed with cold toluene (10 mL), and dried under vacuum to yield 0.52 g (65%) of product as dark green needles. ^{1}H NMR (toluene-d_8) δ 4.75 (t, 4 H, *J* = 2.8 Hz), 3.97 (t, 4 H, *J* = 2.8 Hz), 1.87 (s, 30 H). Anal. Calcd for $C_{30}H_{38}Cl_2Zr_2$: C, 55.26; H, 5.87; Cl, 10.88. Found: C, 55.19; H, 5.75; Cl, 10.74.

(η^5:η^5-$C_{10}H_8$)[Cp*ZrCl]$_2$(OCH$_2$) (6). On a high-vacuum gas-handling line, a solution of hydrido chloride complex 4 (400 mg, 0.61 mmol) in toluene (30 mL) was stirred under CO (700 Torr) for 17 h. The solvent and excess CO were removed under vacuum, and the resulting yellow powder was recrystallized from hot toluene to yield small crystals of the toluene solvate. These were freed of toluene by heating at 80 °C under vacuum for 24 h to yield 210 mg (50%) of 6 as a bright yellow powder. Mp 219–221 °C; ^{1}H NMR (toluene-d_8, 25 °C) δ 6.82 (m, 2 H), 6.36 (m, 2 H), 5.38 (m, 2 H), 5.14 (m, 2 H), 2.47 (br s, 2 H, OCH$_2$), 1.82 (s, 30 H). ^{13}C NMR (toluene-d_8, complex prepared from ^{13}CO) δ 63.3 (t, $^1J_{C-H}$ = 151 Hz). Anal. Calcd for $C_{31}H_{40}Cl_2OZr_2$: C, 54.59; H, 5.91; Cl, 10.40. Found: C, 54.61; H, 6.01; Cl, 10.40.

(η^5:η^5-$C_{10}H_8$)[Cp*Zr(OCH$_2$)]$_2$ (7). On a high-vacuum gas-handling line, a suspension of tetrahydride complex 3 (250 mg, 0.43 mmol) in toluene (30 mL) was stirred under CO (700 Torr) for 24 h. Solvent was removed from the resulting bright yellow suspension under vacuum to give a yellow powder. Crystals were obtained by saturating a solution in toluene (40 mL) at the boiling point and cooling it slowly to room temperature. These were isolated by filtration, washed with toluene (5 mL), and dried under vacuum to yield 240 mg (86%) of analytically pure 7. Mp 343 °C dec; ^{1}H NMR (toluene-d_8) δ 6.62 (m, 2 H), 5.77 (m, 2 H), 5.67 (m, 2 H), 4.76 (m, 2 H), 3.14 (d, 2 H, *J* = 0.8 Hz), 2.68 (d, 2 H, *J* = 0.8 Hz), 1.80 (s, 30 H); ^{13}C NMR (toluene-d_8, complex prepared from ^{13}CO) δ 70.3 (t, $^1J_{C-H}$ = 150 Hz). Anal. Calcd for $C_{32}H_{42}O_2Zr_2$: C, 59.95; H, 6.60. Found: C, 59.79; H, 6.58.

X-ray Structure of 7. Crystals of 7 grown from toluene were mounted on glass fibers and coated with epoxy. Crystal data are given in Table I. Complete details of the experimental conditions for data collection and structure refinement are given in the supplementary material. The structure was solved by direct methods and refined by using full-matrix least-squares techniques. The carbon atoms of the bridging formaldehyde ligands are disordered. Their occupancies were determined by least-squares

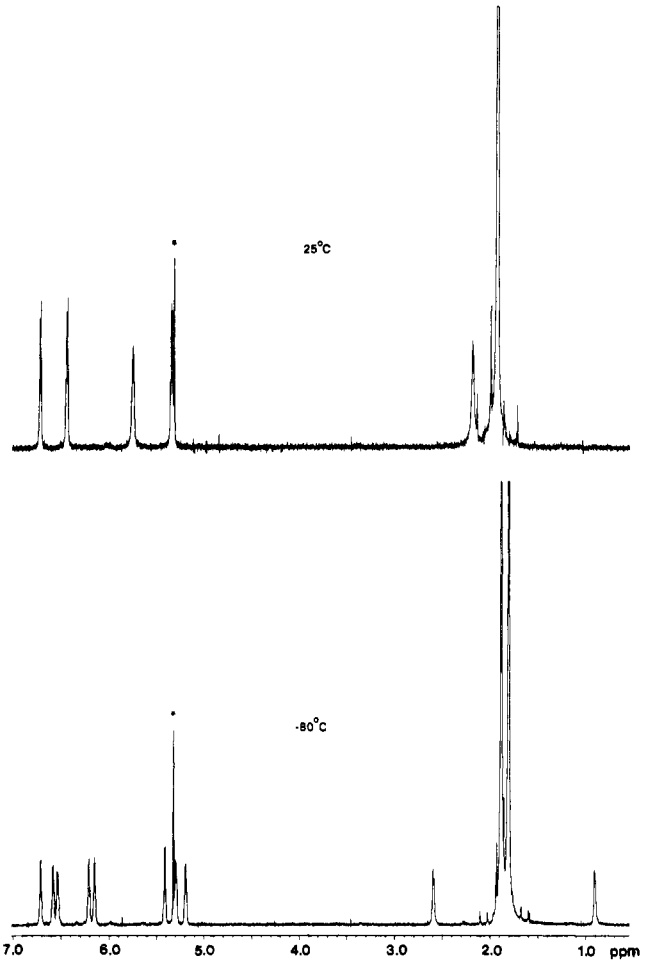


Figure 1. Variable-temperature ^1H NMR spectra of **6** in CD_2Cl_2. The peak marked with an asterisk is due to the residual protons of the solvent.

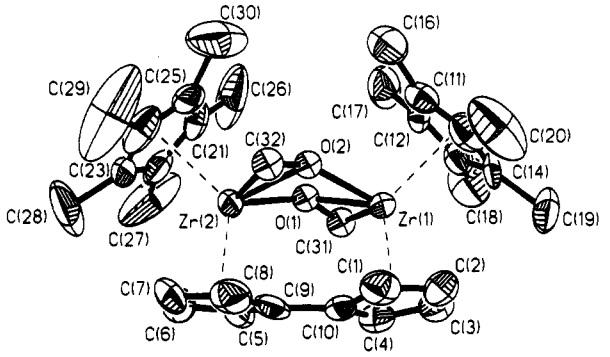


Figure 2. Perspective view of the molecular configuration of $(C_{10}H_8)[Cp^*Zr(OCH_2)]_2$ with the atom numbering scheme for non-hydrogen atoms. The thermal elipsoids are scaled to enclose 50% probability.

techniques. All non-hydrogen atoms except the two lower occupancy disordered atoms were refined anisotropically. Hydrogen atoms on the disordered carbons were not located. The final model included all other hydrogen atoms in fixed, idealized positions. A perspective view of the molecule showing the atom numbering scheme is shown in Figure 2. Atomic coordinates and equivalent isotropic displacement parameters are presented in Table II. Selected bond lengths and angles are presented in Table III. Full tables of derived results are included in the supplementary material.

Results and Discussion

Fulvalene dianion, prepared in THF and then freed of THF under vacuum, reacts with $(Cp^*ZrCl_3)_x$[29] in refluxing toluene to yield the dinuclear tetrachloride complex **1** according to eq 1. In the past, we have prepared me-

$$(C_{10}H_8)Li_2 + 2(Cp^*ZrCl_3)_x \rightarrow (\eta^5{:}\eta^5\text{-}C_{10}H_8)[Cp^*ZrCl_2]_2 + 2LiCl \quad (1)$$

tallofulvalene complexes from the fulvalene dianion prepared and reacted in situ in THF or 1,2-dimethoxyethane (DME).[16d,17] When such preparations were treated with $(Cp^*ZrCl_3)_x$ and heated to reflux, the only zirconium-containing products isolated were $Cp^*ZrCl_3(THF)_2$ or $Cp^*ZrCl_3(DME)$. This is in accord with the strong Lewis-acid character of $(Cp^*ZrCl_3)_x$ and its effect on substitution reactions found by Wolczanski and Bercaw.[29]

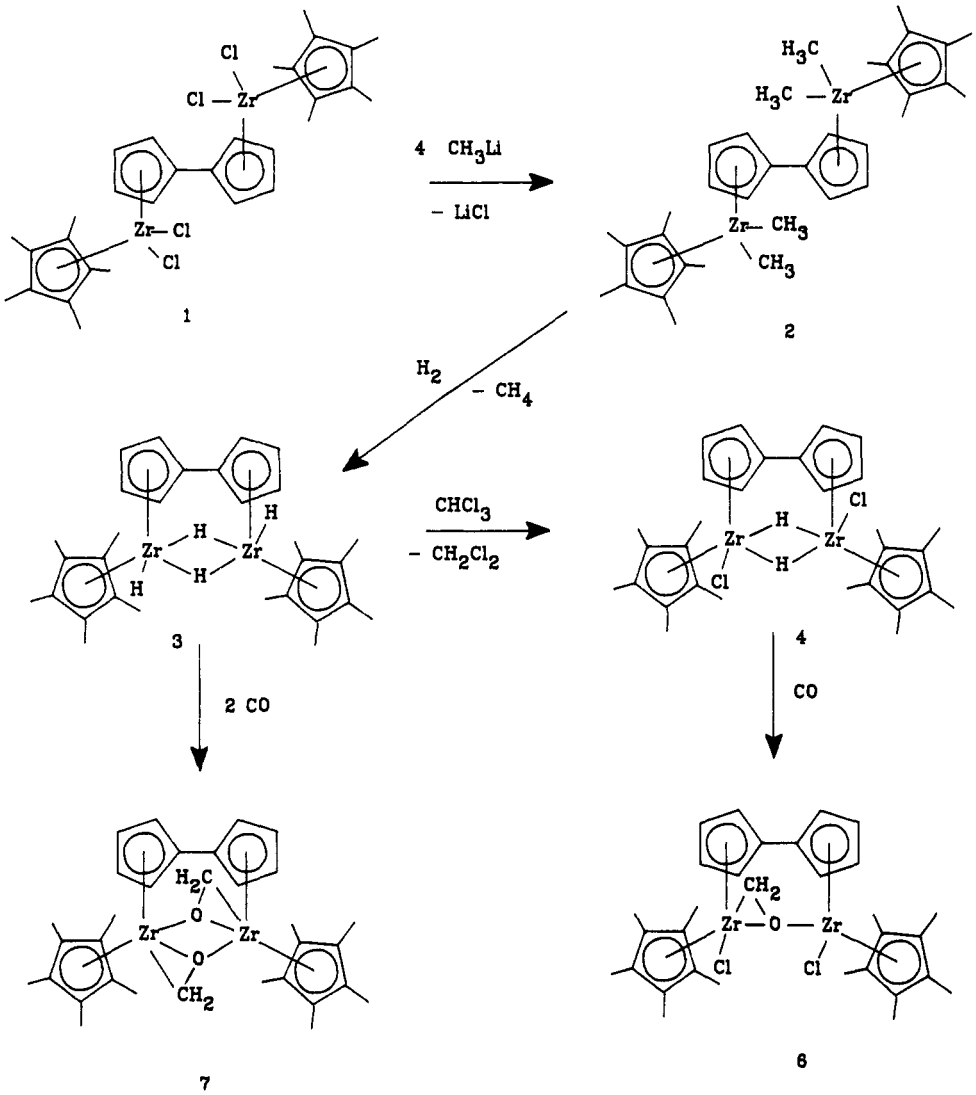
In order to better control the stoiochiometry of fulvalene dianion reactions and to avoid the inconvenience of removing THF completely from the in situ preparation and replacing it with toluene, a method for isolation of a pure salt of the dianion was desired. This was accomplished by preparing a heptane solution of dihydrofulvalene using the method of Vollhardt and Weidman[14] and then deprotonating with *n*-BuLi. This afforded $(C_{10}H_8)Li_2$ in good yield as a white, air-sensitive powder, which was characterized by determination of its equivalent weight. This material reacts with $(Cp^*ZrCl_3)_x$ in toluene to produce **1** in good yield. Complex **1** is soluble in chlorinated hydrocarbon solvents and can be recrystallized from hot

Table II. Atomic Coordinates[a] (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for $(C_{10}H_8)(C_5Me_5)_2Zr_2(OCH_2)_2$

	x/a	y/b	z/c	U(eq)[b]
Zr1	2432 (1)	6622	8366 (1)	48 (1)*
Zr2	2036 (2)	5553 (1)	5664 (1)	52 (1)*
O1	636 (8)	6175 (4)	6913 (6)	40 (2)*
O2	3287 (8)	5478 (5)	7502 (6)	37 (2)
C31#	−247 (18)	6891 (9)	7237 (14)	50 (6)*
C32#	4487 (17)	5102 (10)	6961 (14)	50 (6)*
C31′#	−514 (52)	6485 (27)	6018 (36)	46 (11)
C32′#	4886 (50)	5465 (29)	8157 (34)	42 (10)
C1	4945 (15)	7299 (8)	7787 (11)	64 (5)*
C2	4719 (15)	7766 (8)	8786 (12)	60 (5)*
C3	3239 (21)	8207 (8)	8469 (13)	71 (6)*
C4	2608 (16)	8034 (8)	7249 (12)	62 (5)*
C5	1801 (17)	7054 (8)	4751 (10)	60 (5)*
C6	1906 (22)	6519 (11)	3796 (12)	73 (6)*
C7	3457 (23)	6157 (10)	4036 (13)	82 (7)*
C8	4360 (19)	6459 (8)	5177 (13)	73 (6)*
C9	3267 (15)	7026 (8)	5599 (10)	57 (5)*
C10	3643 (14)	7474 (7)	6814 (10)	48 (4)*
C11	2393 (15)	5512 (9)	10050 (9)	49 (4)*
C12	868 (16)	5863 (8)	9801 (10)	52 (5)*
C13	935 (13)	6744 (8)	10130 (9)	54 (4)*
C14	2619 (20)	6938 (9)	10660 (9)	70 (5)*
C15	3524 (15)	6151 (11)	10564 (12)	69 (6)*
C16	2860 (21)	4573 (9)	9918 (12)	96 (7)*
C17	−728 (17)	5371 (10)	9369 (12)	95 (7)*
C18	−532 (21)	7359 (11)	10111 (16)	122 (9)*
C19	3142 (24)	7777 (12)	11280 (13)	110 (8)*
C20	5362 (18)	6088 (14)	11087 (15)	137 (10)*
C21	−202 (14)	4403 (8)	5559 (10)	52 (4)*
C22	−346 (18)	4758 (7)	4384 (12)	71 (5)*
C23	1042 (25)	4479 (9)	3959 (10)	83 (7)*
C24	2017 (17)	4021 (9)	4840 (17)	78 (7)*
C25	1209 (18)	3983 (8)	5817 (11)	60 (5)*
C26	−1472 (25)	4408 (14)	6304 (18)	166 (12)*
C27	−1806 (23)	5244 (10)	3653 (20)	183 (12)*
C28	1167 (37)	4547 (16)	2650 (14)	238 (19)*
C29	3503 (20)	3537 (14)	4719 (23)	220 (18)*
C30	1895 (30)	3404 (12)	6933 (16)	205 (14)*

[a] Atoms have occupancies of 1.0 except as marked with #: C31, 0.75; C32, 0.75; C31′, 0.25; C32′, 0.25. [b] For atoms marked with *, the equivalent isotropic U is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Scheme I



chlorobenzene or 1,2-dichloroethane to give bright yellow, air-stable crystals.

Proton NMR spectroscopy provides a convenient tool for the characterization of fulvalene complexes. The presence of a plane of symmetry containing the carbons linking the five-membered rings gives rise to an AA′BB′ spin system, which is generally observed as a pair of pseudotriplets. When this plane is absent, four multiplets of an ABCD spin system are observed. The ^{1}H NMR spectrum of 1 shows the expected pair of triplets and a sharp singlet due to the methyl groups on the equivalent Cp* ligands.

Complex 1 reacts cleanly with 4 equiv of CH_3Li in diethyl ether or toluene to yield the tetramethyl complex 2, as shown in Scheme I. Colorless needles of 2 were obtained by recrystallization from toluene. The complex is also soluble in ether and sparingly so in hexane. The ^{1}H NMR spectrum of 2 shows a singlet at δ −0.39 that is characteristic of methyl groups bound to zirconium,[30] in addition to a pair of triplets and a singlet due to the fulvalene and Cp* ligands, respectively.

A number of methods have been used to prepare hydride complexes of group 4 metals. These include reaction of chloride complexes with aluminum hydrides,[31,35] boron hydrides,[32] or butyllithium under hydrogen,[24,29] hydrogenolysis of alkyl groups from suitable alkyl-substituted precursors,[29] and oxidative addition of hydrogen to low-valent complexes.[30b] A number of these methods were tried for converting the chloride complex 1 to the hydride complex 3. The best method was found to be hydrogenolysis of the methyl ligands in 2 at elevated pressure and temperature (300 psi, 80 °C). This yields the tetrahydride complex 3 as a white, microcrystalline solid in high yield. Complex 3 is also produced when 1 is treated with *n*-butyllithium (4 equiv) under hydrogen. This initially gives an intermediate, tentatively identified as the mixed butyl hydride $Cp^*_2(\eta^5{:}\eta^5\text{-}C_{10}H_8)Zr_2(H)_2(Bu)_2$,[33] which is converted to 3 at higher temperature and pressure. The hydride produced by this route was less pure, however, and was often contaminated with green or blue impurities. The infrared spectrum of 3 shows two strong, broad absorptions at 1562 and 1255 cm^{-1}, assigned to terminal and bridging

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Table III. Selected Bond Distances (Å) and Bond Angles (deg) for $(C_{10}H_8)[Cp^*Zr(OCH_2)]_2$ (7)[a]

	Bond Distances		
Zr1–Zr2	3.415 (2)	Zr1–O1	2.098 (6)
Zr1–O2	2.193 (7)	Zr1–C31	2.37 (1)
Zr1–C32′	2.74 (4)		
Zr1–Cp*1	2.265	Zr1–ful1	2.244
Zr2–O1	2.206 (7)	Zr2–O2	2.128 (6)
Zr2–C32	2.36 (1)	Zr2–C31′	2.64 (4)
Zr2–Cp*2	2.247	Zr2–ful2	2.230
O1–C31	1.41 (2)	O1–C31′	1.33 (4)
O2–C32	1.39 (2)	O2–C32′	1.38 (4)
	Bond Angles		
O1–Zr1–O2	68.4 (2)	O1–Zr1–C31	36.2 (4)
O2–Zr1–C31	104.6 (4)	O1–Zr1–C32′	98.3 (8)
O2–Zr1–C32′	30.0 (8)	C31–Zr1–C32′	134.3 (9)
Cp*1–Zr1–ful1	128.7	O1–Zr2–O2	67.7 (2)
O1–Zr2–C32	103.2 (4)	O2–Zr2–C32	35.6 (4)
O1–Zr2–C31′	30.2 (9)	O2–Zr2–C31′	97.7 (9)
Cp*2–Zr2–ful2	128.7	Zr1–O1–Zr2	105.0 (3)
Zr1–O1–C31	82.3 (6)	Zr2–O1–C31	150.1 (8)
Zr1–O1–C31′	139.9 (18)	Zr2–O1–C31′	93.4 (19)
Zr1–O2–Zr2	104.4 (3)	Zr1–O2–C32	148.1 (8)
Zr2–O2–C32	81.3 (6)	Zr1–O2–C32′	97.7 (19)
Zr2–O2–C32′	138.7 (18)	Zr1–C31–O1	61.5 (6)
Zr2–C32–O2	63.1 (6)	Zr2–C31′–O1	56.4 (16)
Zr1–C32′–O2	52.4 (15)		

[a] The Zr1–Zr2 contact, which is not a bond, is included for purposes of discussion. The centroids of the cyclopentadienyl and fulvalene rings are referred to as Cp*1 (C11 to C15), Cp*2 (C21 to C25), ful1 (C1 to C4 and C10), and ful2 (C5 to C9).

metal hydride stretches, respectively. These shift to 1125 and 902 cm^{-1} in the tetradeuteride, prepared from **2** and D_2. These values are very close to those reported for $(Cp^*CpZrH_2)_2$ (1540, 1270 cm^{-1}),[29] which is the analogous complex with unlinked Cp rings.

Proton NMR spectra of **3** are temperature-dependent and indicate that exchange of hydride ligands between bridging and terminal sites occurs on the NMR time scale. Although hampered by the low solubility of **3**, the low-temperature spectrum (−52 °C) in toluene shows two broad triplets at δ 4.02 and −1.68 ($^2J_{H-H}$ = 8.1 Hz) due to the terminal and bridging hydrides, respectively. In addition, the spectrum shows an ABCD pattern for the protons on the fulvalene ligand, consistent with the lower symmetry in this complex, and a sharp singlet due to the methyl group on the Cp* ligand. At high temperature (120 °C), a broad singlet (δ 1.25) is observed for the four rapidly exchanging hydride ligands, and the fulvalene protons appear as a pair of triplets (δ 5.89, 4.98, J = 2.7 Hz) because of the introduction of an apparent mirror plane in the molecule. The activation energy for the process, estimated from the chemical shift difference of the hydride ligands in the low-temperature spectrum and the coalescence temperature (+20 °C), is 13 ± 1 kcal/mol.[34]

These data are consistent with the structure for **3** depicted in Scheme I with two bridging and two terminal hydride ligands. This type of structure has been confirmed by X-ray crystallography for $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$[31] and postulated for other zirconium hydride dimers containing substituted Cp ligands.[29] A similar dinuclear hydride complex with a bridging $(C_5H_4)_2Si(CH_3)_2^{2-}$ ligand has been reported.[35]

The tetrahydride complex **3** reacts with chloroform under mild conditions to selectively replace two hydride ligands, presumably the terminal set, with chlorides to produce the hydrido chloride complex **4**. When this reaction is monitored by ^1H NMR spectroscopy, clean conversion of **3** to **4** is observed and methylene chloride is the observed coproduct. Complex **4** is stable toward further reaction in the presence of excess chloroform at room temperature. Further reaction of **4** with chloroform is observed at 80 °C where, over a period of several hours, **1** is produced.

The ^1H NMR spectrum of **4** shows the expected ABCD pattern of resonances for the fulvalene protons and a singlet for the Cp* ligand. The hydride resonance appears at δ +0.95 as a broad singlet. The infrared spectrum of **4** shows a strong, broad zirconium hydride stretch at 1360 cm^{-1}, which shifts to 976 cm^{-1} for the deuteride. These data make the assignment of the structure of **4** somewhat ambiguous because the chemical shift of the hydride and the frequency of the metal hydride stretch are intermediate between those observed for bridging and terminal hydrides in **3** and other known systems.[29,31] The structure with bridging hydride ligands depicted in Scheme I is assigned on the basis of the relatively low value of the metal hydride stretching frequency and the known propensity of zirconium hydride complexes to form strong hydride bridges.[29] Reddy and Petersen have reported the synthesis and structure of $[(\eta^5\text{-}C_5H_4)_2SiMe_2][(\eta^5\text{-}C_5H_5)ZrCl(\mu\text{-}H)]_2$,[35] a dinuclear hydrido chloride complex similar to **4**. They observed the metal hydride stretch at 1390 cm^{-1} and the hydride chemical shift of δ −0.06 for this complex, and confirmed the presence of bridging hydride ligands by X-ray crystallography. These data and that for **4** show that infrared stretching frequency is a reasonable criterion for determining bridging versus terminal hydride bonding modes for zirconium complexes but that hydride chemical shifts are more variable and should be used more cautiously when assigning hydride bonding modes.

Complex **4** is stable to thermally induced loss of H_2 in solution and the solid state up to 110 °C. Photochemically induced elimination of H_2 is a facile process, however. Photolysis of **4** in an NMR tube with a low-pressure mercury lamp for 8 h produces a dark green solution containing a new complex, **5**. The ^1H NMR spectrum of **5** shows a pair of triplets (δ 4.75, 3.97, J = 2.8 Hz) for the protons of the fulvalene ligand, indicating that the molecule possesses a mirror plane lengthwise through the fulvalene ligand. This simple NMR spectrum, the dark color, and the elemental analysis support the formulation of **5** as a chloro-bridged complex of Zr(III). An analogous complex containing unsubstituted Cp ligands results from the comproportionation of Cp_2ZrCl_2 and $Cp_2Zr(PMe_3)_2$ and has been structurally characterized.[2] Complex **5** can be prepared on a large scale by reducing **1** with 2 equiv of sodium amalgam in THF.

Complex **4** reacts with excess CO slowly at room temperature according to the reaction shown in Scheme I, to yield the bridging formaldehyde complex **6**. The ^{13}C NMR spectrum of **6** shows a resonance due to the aldehyde carbon at δ 63.3 ppm (t, $^1J_{C-H}$ = 151 Hz), which is in good agreement with the values found by Floriani for $(Cp_2ZrCl)_2(\mu\text{-}CH_2O)$,[20,21] which was structurally characterized, and by Erker for similar complexes with bridging alkyl and aryl aldehydes.[22,36] Like these cyclopentadienyl complexes, **6** is fluxional on the NMR time scale, undergoing a dyotropic rearrangement[25b,37] in which the aldehyde carbon pivots on the bridging oxygen and moves back and forth between the two zirconium atoms. The high- and low-temperature ^1H NMR spectra of **6** are shown in Figure 1. The low-temperature spectrum shows eight multiplets for the protons of the inequivalent rings of the fulvalene ligand, two Cp* resonances, and an AX pattern with small coupling for the two protons of the bridging formaldehyde group, consistent with the low symmetry of the locked

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structure. The high-temperature spectrum is consistent with the presence of a mirror plane bisecting the carbon–carbon bond linking the fulvalene rings and a line between the two metal atoms, except the protons on the aldehyde carbon appear as a single resonance instead of the expected AX pattern. This indicates that there is rapid rotation about the C–O bond at high temperature that exchanges these protons between the two sites. This is in contrast to the results obtained for the complexes $(Cp_2ZrCl)_2(\mu$-OCHR), which show the rearrangement to be stereospecific at carbon with no rotation about the C–O bond even at high temperature.[36,38] This difference is attributed to the steric bulk of the substituents on the aldehyde; hydrogen is small enough to allow rotation whereas larger substituents do not. Complex **6** is the first unsubstituted aldehyde complex with low enough symmetry to observe this effect.

The activation barrier for this process ($\Delta G^{\ddagger}_{TC}$), obtained from the separation of the Cp* signals in the low-temperature spectrum and the coalescence temperature (−50 °C),[34] is 11.2 kcal/mol.

Complex **6** reacts further with carbon monoxide under more forcing conditions. When **6** is sealed in an NMR tube with excess CO and heated to 80 °C, a clean reaction that produces a new product is observed. The ^{1}H NMR spectrum of this product shows four multiplets for the protons of the fulvalene ligand, a singlet due to the Cp* ligand, and a new singlet at δ 6.06. When this product is prepared from the hydride **4** and ^{13}C-labeled carbon monoxide, the resonance at δ 6.06 is observed as a symmetrical 10-line pattern of an AA′XX′ spin system. This is consistent with the formulation of this product as a symmetrical enediolate complex.[23,30b] Analysis of the AA′XX′ spectrum[39] yields values of 2.7 Hz for $^3J_{H-H}$ and 20.7 Hz for $^2J_{C-H}$, indicating that the two carbon monoxide molecules are coupled to form a *cis*-enediolate ligand. These data combined with the symmetry deduced from the NMR spectrum indicate that the enediolate ligand bridges the two metal atoms with one oxygen bound to each metal.

The tetrahydride complex **3** reacts with excess carbon monoxide slowly at room temperature according to the reaction shown in Scheme I to yield a sparingly soluble, yellow complex with two bridging formaldehyde ligands, **7**. The NMR spectra of this complex are consistent with this formulation. The formaldehyde ligands are equivalent and give rise to a signal in the ^{13}C NMR at δ 70.3 (t, J_{CH} = 149 Hz). The protons of the formaldehyde ligands give rise to an AX pattern in the ^{1}H NMR spectrum with a small coupling constant (δ 2.68, 3.14, d, $^2J_{H-H}$ = 0.9 Hz).

In order to confirm the presence of two bridging formaldehyde ligands and for the purpose of comparison with the known structures of $[Cp_2Zr(OCH_2)]_2$[40] and $[Cp_2Zr(OCH_2)]_3$,[25] the structure of **7** was determined by X-ray diffraction.

The crystal structure consists of discrete molecules of **7** at general positions in the unit cell. There is no crystallographically imposed symmetry, but the molecule exhibits approximate C_2 symmetry.

The carbon atoms of the $Zr_2(OCH_2)_2$ unit are disordered, partially occupying a site located on the other side of the bridging oxygen atom and bonded to the opposite zirconium atom. Refinement of the occupancy indicates that the configuration shown in Figure 2 is 75% occupied, and the alternate configuration, with the carbon atoms flipped to bond to the opposite metal atoms, is 25% occupied. The lower occupancy atoms C31′ and C32′ did not refine as well as the others, showing larger uncertainties in their positional and thermal parameters and in bond lengths derived from them. The hydrogen atoms on the bridging formaldehyde ligands could not be located and were not included in the final model structure.

The bonding of the fulvalene and Cp* rings to the zirconium centers is typical, in terms of metal–ring distances and ring centroid–Zr–ring centroid angles, of structures of $Cp_2Zr(IV)$ that have been reported.[41] The two rings of the bridging fulvalene ligand are rotated by about 8° relative to one another and bent slightly toward the metals. The influence of the fulvalene ligand on the $Zr_2(OCH_2)_2$ core can be gauged by comparison with the structure of $[Cp_2Zr(OCH_2)]_2$,[40] the analogous complex with unlinked Cp rings. The bond distances that characterize the core are virtually identical in both complexes. However, the metal–metal distance is shorter in **7** than in the complex with unlinked rings, causing the $Zr_2(OCH_2)$ unit to fold along the O1–O2 vector. The planes defined by Zr1, O1, and O2 and Zr2, O1, and O2 intersect at an angle of 146°. In addition, the carbon atoms are bent out of these planes and away from the Cp* ligands, probably due to steric interactions between the aldehyde hydrogens and the hydrogens of the Cp* methyl groups.

Conclusion

We set out to prepare these dinuclear zirconium complexes to compare their reactivity with that of the known cyclopentadienyl analogues. The result observed is that there is very little difference between the fulvalene complexes and the complexes with unlinked cyclopentadienyl rings, in this case. The reaction chemistry of **4** with CO parallels that of $[Cp_2Zr(H)Cl]_x$ and that of **3** is similar to that of $[Cp_2ZrH_2]_x$. The structure of the $Zr_2(OCH_2)_2$ core in **7** is virtually identical with that found in $[Cp_2Zr(OCH_2)]_2$. This comparison shows that, insofar as reaction of the hydrides with CO is concerned, there is little difference between the two classes of complexes. This may be due, in part, to the oligomeric nature of the cyclopentadienyl systems.

We are pursuing other reactions of these hydrides where distinctly different reactivities are observed for dinuclear and mononuclear systems.

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Supplementary Material Available: Tables of crystal data, solution and refinement details, bond lengths and angles, anisotropic displacement parameters, and H atom coordinates for **7** (11 pages); a list of observed and calculated structure factors for **7** (13 pages). Ordering information is given on any current masthead page.

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