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Competitive CH Activation in (Pentamethylcyclopentadienyl)(cyclooctatetraene)alkylzirconium Compounds $\text{Cp}^*\text{Zr}(\text{COT})\text{R}$. Selective Formation of Fulvene or Cyclooctatrienyl Ligands. Molecular Structure of $\text{Cp}^*\text{Zr}(\mu\text{-}\eta^8$

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Competitive CH Activation in (Pentamethylcyclopentadienyl)(cyclooctatetraene)alkylzirconium Compounds $\text{Cp}^*\text{Zr}(\text{COT})\text{R}$. Selective Formation of Fulvene or Cyclooctatrienyne Ligands. Molecular Structure of $\text{Cp}^*\text{Zr}(\mu\text{-}\eta^8\text{:}\eta^2\text{-C}_8\text{H}_6)\text{ZrCp}^*(\eta^4\text{-C}_8\text{H}_8)$, a Dinuclear Zwitterionic Zirconium Complex with a Bridging Cyclooctatrienyne Ligand

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Thermolysis of $\text{Cp}^*\text{Zr}(\text{COT})\text{R}$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$, $\text{COT} = \eta^8\text{-C}_8\text{H}_8$, $\text{R} = \text{CH}_2\text{SiMe}_3$, Me) proceeds via a double hydrogen abstraction from a cyclooctatetraene ligand to give RH and $\text{Cp}^*\text{Zr}(\mu\text{-}\eta^8\text{:}\eta^2\text{-C}_8\text{H}_6)\text{ZrCp}^*(\eta^4\text{-C}_8\text{H}_8)$ as the kinetic product. $\text{Cp}^*\text{Zr}(\mu\text{-}\eta^8\text{:}\eta^2\text{-C}_8\text{H}_6)\text{ZrCp}^*(\eta^4\text{-C}_8\text{H}_8)$ undergoes a thermally induced hydrogen transfer from the pentamethylcyclopentadienyl ligands to the cyclooctatetraenediyl ligand to give the thermodynamic product FvZrCOT ($\text{Fv} = \eta^6\text{-C}_5\text{Me}_4\text{-CH}_2$). For $\text{Cp}^*\text{Zr}(\text{COT})\text{R}$ ($\text{R} = \text{CH}_2\text{Ph}$) a different thermolysis reaction was observed, in which FvZrCOT was the major product at low temperatures, together with some $\text{Cp}^*\text{Zr}(\mu\text{-}\eta^8\text{:}\eta^2\text{-C}_8\text{H}_6)\text{ZrCp}^*(\eta^4\text{-C}_8\text{H}_8)$. The latter does not convert into the thermodynamic product at the temperature of thermolysis, indicating an alternative, direct, thermal decomposition pathway to FvZrCOT for $\text{R} = \text{CH}_2\text{Ph}$, with preferred hydrogen abstraction from the sp^3 carbon of the pentamethylcyclopentadienyl ligand. $\text{Cp}^*\text{Zr}(\mu\text{-}\eta^8\text{:}\eta^2\text{-C}_8\text{H}_6)\text{ZrCp}^*(\eta^4\text{-C}_8\text{H}_8)$ crystallizes in the monoclinic space group $\text{P}2_1/n$ with $a = 8.324$ (2) Å, $b = 15.966$ (3) Å, $c = 22.647$ (3) Å, $\beta = 92.56$ (1)°, $V = 3007$ (1) Å³, and $Z = 4$. The molecular structure shows an unprecedented cyclooctatrienyne ligand, bridged asymmetrically between the Zr atoms. The formulation as a cyclooctatrienyne complex is formal; the actual bonding of the ligand is as a dimetalated η^8 -cyclooctatetraene-1,2-diyl. The diamagnetism of $\text{Cp}^*\text{Zr}(\mu\text{-}\eta^8\text{:}\eta^2\text{-C}_8\text{H}_6)\text{ZrCp}^*(\eta^4\text{-C}_8\text{H}_8)$ implies a zwitterionic complex in which a 16-electron zirconium center $[\text{Cp}^*\text{Zr}(\text{COT})]^+$ is connected to another 16-electron center $[\text{Cp}^*\text{Zr}(\eta^4\text{-C}_8\text{H}_8)\text{R}_2]^-$ through a bridging η^8 -cyclooctatetraene-1,2-diyl ligand.

Introduction

Selective, intramolecular CH activation appears to be a useful synthetic method for the preparation of various ligand systems, starting from conveniently accessible ligands. Cyclopentadienyl and pentamethylcyclopentadienyl ligands have been reported to give fulvalene or fulvene¹ systems, and alkyl or aryl ligands may lose hydrogen at α or β positions to form alkylidene, olefin, or aryne complexes.² Heteroatom aromatic ligands such as pyridine can be metalated at the position adjacent to the heteroatom.³ Our group is interested in developing new synthetic routes toward functionalized (peralkyl)cyclopentadienyl systems of early transition metals and lanthanide elements starting from fulvene compounds.^{1d,e,4}

We decided to investigate routes to group 4 fulvene complexes of the type FvML_n ($\text{Fv} = \eta^6\text{-C}_5\text{Me}_4\text{CH}_2$) using mono(pentamethylcyclopentadienyl) compounds $\text{Cp}^*\text{M}(\text{COT})\text{R}$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$, $\text{COT} = \eta^8\text{-C}_8\text{H}_8$, $\text{R} = \text{alkyl}$) as starting material utilizing thermal extrusion of RH , followed by selective activation of the sp^3 carbon of the pentamethylcyclopentadienyl ligand. It is not easy to predict from which ligand hydrogen abstraction will occur. A strict preference for abstraction from an sp^2 or from an sp^3 carbon atom has not yet been observed. Thermolysis of Cp^*ZrPh_2 initially proceeds with hydrogen abstraction from the phenyl ligand and formation of the benzyne compound $\text{Cp}^*\text{Zr}(\eta^2\text{-C}_6\text{H}_4)$, which can be trapped with

ethylene to give $\text{Cp}^*\text{Zr-}o\text{-C}_6\text{H}_4\text{CH}_2\text{CH}_2$. Further thermolysis of $\text{Cp}^*\text{Zr}(\eta^2\text{-C}_6\text{H}_4)$ results in an intramolecular hydrogen shift and formation of the fulvene complex Cp^*FvZrPh . A similar reaction is also found for the thermolysis of $\text{Cp}^*\text{CpTi}(\text{Me})\text{Ph}$, which proceeds via a $\text{Cp}^*\text{CpTi}(\eta^2\text{-C}_6\text{H}_4)$ intermediate which can be trapped with CO_2 .⁶ In these cases hydrogen abstraction from an sp^2 carbon atom is kinetically favored. The final fulvene complexes, which are generated by hydrogen abstraction

(1) (a) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* 1972, 94, 1219. (b) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* 1982, 1, 1629. (c) Pattiasina, J. W. Thesis, R. U. Groningen, 1988. (d) Pattiasina, J. W.; Hissink, C. E.; De Boer, J. L.; Meetsma, A.; Teuben, J. H.; Spek, A. L. *J. Am. Chem. Soc.* 1985, 107, 7758. (e) Pattiasina, J. W.; Van Bolhuis, F.; Teuben, J. H. *Angew. Chem.* 1987, 99, 342. (f) Luinstra, G. A.; Ten Cate, L. C.; Heeres, H. J.; Pattiasina, J. W.; Meetsma, A.; Teuben, J. H. *Organometallics* 1991, 10, 3227. (g) Abugideiri, F.; Kelland, M. A.; Poll, R.; Rheingold, A. L. *Organometallics* 1992, 11, 1309. (h) Gibson, V. C.; Kee, T. P.; Carter, S. T.; Sanner, R. D.; Clegg, W. *J. Organomet. Chem.* 1991, 418, 197.

(2) Rothwell, I. P. In *Davies, J. A.; Watson, P. L.; Liebman, J. F.; Greenberg, A. Selective Hydrocarbon Activation*; VCH Publishers: New York, 1990; pp 43-78.

(3) Guram, A. S.; Jordan, R. F. *Organometallics* 1991, 10, 3470.

(4) Fandos, R.; Meetsma, A.; Teuben, J. H. *Organometallics* 1991, 10, 2665.

(5) Schock, L. E.; Brock, C. P.; Marks, T. J. *Organometallics* 1987, 6, 232.

from a pentamethylcyclopentadienyl ligand, are the thermodynamic products. In contrast, the thermolysis of Zr(COT)Mes₂ (Mes = 2,4,6-Me₃C₆H₂) shows a different reaction pathway. In this case the cyclooctatetraene ligand is not involved and the hydrogen abstraction occurs exclusively from the sp³ carbon atoms of the methyl groups of the mesityl ligands.⁷ The thermolysis of Cp*₂Hf(CH₂-Ph)₂ is even more complex and results in hydrogen abstraction from the α-carbon atom giving Cp*₂Hf=CHPh, which rearranges via Cp*FvHfCH₂Ph to Cp*₂HfCH₂-o-C₆H₄. In this case the preference for hydrogen abstraction from an sp² or sp³ carbon atom is not clear.⁸

In this paper we describe a study of the thermolysis of compounds Cp*Zr(COT)R (R = Me, CH₂SiMe₃, CH₂Ph) aimed at developing a synthesis of fulvene complexes, FvZrCOT.

Results and Discussion

Thermolysis of Cp*Zr(COT)R Monitored by ¹H-NMR. Thermolysis of Cp*Zr(COT)CH₂SiMe₃ in benzene-d₆ was complete in about 6 h at 170 °C. A quantitative amount of Me₄Si was formed, together with red-brown, poorly soluble Cp*Zr(μ-η⁸:η²-C₈H₆)ZrCp*(η⁴-C₈H₈) (vide infra). On prolonged heating (20 h, 170 °C), the deposited material dissolved completely to give an intensely colored, dark-red solution of FvZrCOT (vide infra). This second transformation was not quantitative; FvZrCOT was formed in ca. 85% yield, and no other products could be identified. Thermolysis of Cp*Zr(COT)Me proceeded significantly more slowly under the conditions used for the (trimethylsilyl)methyl analogue, and the process was less clean. Eventually, methane and FvZrCOT appeared to be the main products, however.

The benzyl analogue Cp*Zr(COT)CH₂Ph behaved very differently. It proved to be much less thermally stable than the other complexes studied and was converted completely within 1 h at 110 °C, giving a quantitative amount of toluene and a mixture of Cp*Zr(μ-η⁸:η²-C₈H₆)ZrCp*(η⁴-C₈H₈) and FvZrCOT. At 110 °C no indication was obtained for conversion of Cp*Zr(μ-η⁸:η²-C₈H₆)ZrCp*(η⁴-C₈H₈) into FvZrCOT; this only was observed at much higher temperatures (>170 °C). When the thermolysis was carried out at lower temperatures, the ratio of insoluble material and FvZrCOT changed in favor of the latter. This observation clearly indicates that for Cp*Zr(COT)CH₂Ph two independent thermolysis pathways compete. Both produce toluene, most probably through hydrogen abstraction from either the pentamethylcyclopentadienyl or the cyclooctatetraene ligand. The difference is that one pathway gives FvZrCOT directly and is unique for Cp*Zr(COT)R with R = CH₂Ph, while the other first forms Cp*Zr(μ-η⁸:η²-C₈H₆)ZrCp*(η⁴-C₈H₈) and is similar to the thermolysis reactions of compounds Cp*Zr(COT)R with R = CH₂SiMe₃ and Me.

Other compounds Cp*Zr(COT)R (R = H, Ph, CH=CH₂) showed a completely different behavior on heating. The products obtained for R = Me, CH₂SiMe₃, and CH₂Ph were not formed in other than minor amounts; instead, transfer of R occurred to the cyclooctatetraene ligand, to

Scheme I. Decomposition Pathway of Cp*Zr(COT)R (R = CH₂SiMe₃, Me)

produce (pentamethylcyclopentadienyl)cyclooctatrienyl zirconium complexes Cp*Zr(η⁷-C₈H₈R). A detailed study of this process will be reported in a following paper.⁹

These results indicate that thermolysis of Cp*Zr(COT)R proceeds for R = Me and CH₂SiMe₃ via two separate steps: first a double hydrogen abstraction from a cyclooctatetraene ligand and formation of the dinuclear complex Cp*Zr(μ-η⁸:η²-C₈H₆)ZrCp*(η⁴-C₈H₈) as the kinetic product and then hydrogen transfer from both Cp* groups to the cyclooctatrienyl ligand and formation of thermodynamic product, FvZrCOT (Scheme I).

The formation of Cp*Zr(μ-η⁸:η²-C₈H₆)ZrCp*(η⁴-C₈H₈) is a novel process. To achieve the double abstraction of hydrogen from one cyclooctatetraene ligand, a quite complicated mechanism has to be invoked. Two molecules of Cp*Zr(COT)R have to come together and form RH by metalation of a cyclooctatetraene ligand e.g. through σ-bond metathesis, followed by subsequent extrusion of another molecule of RH by intramolecular nucleophilic attack by R⁻ on the metalated eight-membered ring. The formation of a complex of a, so far unknown, cyclooctatrienyl ligand is unprecedented. Moreover, abstraction of hydrogen from coordinated cyclooctatetraene ligands has not yet been reported.

The conversion of Cp*Zr(μ-η⁸:η²-C₈H₆)ZrCp*(η⁴-C₈H₈) to FvZrCOT by intramolecular transfer of hydrogen from the pentamethylcyclopentadienyl ligands to the cyclooctatrienyl ligand is not so surprising since there are quite a few precedents in early transition metal benzyne chemistry.^{5,6} The thermolysis of Cp*Zr(COT)CH₂Ph proceeds differently, and Cp*Zr(μ-η⁸:η²-C₈H₆)ZrCp*(η⁴-C₈H₈) and FvZrCOT are formed simultaneously. The fact that at 110 °C Cp*Zr(μ-η⁸:η²-C₈H₆)ZrCp*(η⁴-C₈H₈) does not convert into the thermodynamically more stable product indicates a direct route from Cp*Zr(COT)CH₂Ph to FvZrCOT, e.g. homolysis of the Zr-C bond and attack on the pentamethylcyclopentadienyl ligand. It is remarkable that this route dominates at low temperatures over the double metalation of the cyclooctatetraene ligand, but without further detailed kinetic and isotope labeling studies it is impossible to rationalize this.

Molecular Structure of Cp*Zr(μ-η⁸:η²-C₈H₆)ZrCp*(η⁴-C₈H₈). The benzene-insoluble, crystalline red-brown compound obtained on thermolysis could not be identified on the basis of spectroscopic and analytical data. Instead an X-ray diffraction study showed that it is a dinuclear complex, Cp*Zr(μ-η⁸:η²-C₈H₆)ZrCp*(η⁴-C₈H₈), with a bridging cyclooctatrienyl ligand, two regular pentamethylcyclopentadienyl ligands, and a cyclooctatetraene group η⁴-coordinated to one of the zirconium atoms. The

(6) Dros, A. C.; Luinstra, G. A.; Eshuis, J. J. W.; Meetsma, A.; Teuben, J. H. Manuscript in preparation.

(7) Berno, P.; Stella, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. J. Chem. Soc., Dalton Trans. 1990, 2669.

(8) Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. *Organometallics* 1987, 6, 1219.

(9) Sinnema, P.-J.; Van Bolhuis, F.; Teuben, J. H. Manuscript in preparation.

Figure 1. PLUTO drawing of $\text{Cp}^*\text{Zr}(\mu\text{-}\eta^3\text{:}\eta^2\text{-C}_8\text{H}_6)\text{ZrCp}^*(\eta^4\text{-C}_8\text{H}_8)$.

Table I. Selected Bond Distances (Å) and Angles (deg) for $\text{Cp}^*\text{Zr}(\mu\text{-}\eta^3\text{:}\eta^2\text{-C}_8\text{H}_6)\text{ZrCp}^*(\eta^4\text{-C}_8\text{H}_8)$

Bond Distances			
Zr1–Zr2	4.194 (2)	Zr2–C31	2.49 (1)
Zr1–CE(Cp*1) ^a	2.17 (6)	Zr2–C36	2.49 (1)
Zr1–CE(C ₈ H ₆) ^a	1.50 (4)	C–C (Cp*1) ^b	1.38
Zr2–CE(Cp*2) ^a	2.26 (8)	C–Me (Cp*1) ^c	1.49
Zr2–C21	2.203 (8)	C–C (Cp*1) ^b	1.35
Zr2–C22	2.206 (7)	C–Me (Cp*2) ^c	1.44
Zr2–C29	2.414 (9)	C–C (C ₈ H ₆) ^b	1.40
Zr2–C30	2.411 (9)	C–C (C ₈ H ₆) ^b	1.39
Bond Angles			
CE(Cp*1)–Zr1–CE(C ₈ H ₆)	163.6 (5)	C21–Zr2–C22	36.8 (3)
CE(Cp*2)–Zr2–CE(P3) ^d	136.5 (8)	P1 ^d –P2 ^d	12.5 (6)

^a CE denotes ring centroid; Cp*1 = C1–C5, Cp*2 = C11–C15, C₈H₆ = C21–C28. ^b Average bond distance between ring carbon atoms. ^c Average bond distance between C_{ring}–Me in Cp*. ^d P1 = plane through C21, C22, and Zr2; P2 = plane through C21–C28; P3 = plane through C29, C30, C31, and C36.

molecular structure is shown in Figure 1, and relevant geometric data are listed in Table I.

The Zr1–Zr2 distance is 4.194 (2) Å, too long for a metal–metal bond. The cyclooctatrienyne ligand is η^8 -bonded to Zr1 and η^2 -bonded to Zr2. The bond distances Zr2–C21 and Zr2–C22 (2.203 (8) and 2.206 (7) Å) are comparable with Zr–C σ -bonds observed in $\text{Cp}_2\text{ZrMe}_2^{10}$ (2.273 (5) Å), $\text{Cp}_2\text{Zr}(\eta^2\text{-C}_6\text{H}_4)\text{PMe}_3^{11}$ (2.267 (5), 2.248 (5) Å), and $\text{Cp}_2\text{Zr}(\eta^2\text{-C}_6\text{H}_8)^{12}$ (2.165 (3), 2.244 (2) Å). The cyclooctatrienyne ligand is almost planar with maximum deviations of 0.07 (4) Å from the plane. The distances between the carbon atoms of the cyclooctatrienyne ligand and Zr1 vary from 2.34 (1) and 2.39 (1) Å. Although disorder problems make it impossible to discuss the bonding aspects in the cycloalkyne ligand in detail, it can be assumed that the situation is comparable with related systems in which a benzyne ligand is bonded to a transition metal, as observed in $\text{Cp}_2\text{Zr}(\eta^2\text{-C}_6\text{H}_4)\text{PMe}_3^{11}$ and $[\text{Re}(\eta^2\text{-2-MeC}_6\text{H}_3)\text{-(2-MeC}_6\text{H}_4)_2(\text{PMe}_3)_2][\text{I}_5]^{13}$. In the case of $\text{Ni}(\eta^2\text{-C}_6\text{H}_4)((\text{C}_6\text{H}_{11})_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_{11})_2)^{14}$ a short C≡C bond is found while other C–C distances in the ring are equal

but clearly longer. In contrast, $\text{Cp}^*\text{Ta}(\eta^2\text{-C}_6\text{H}_4)\text{Me}_2^{15}$ shows alternating C=C bonds. In the present study, the distance between C21 and C22 of the coordinated alkyne function is 1.39 (1) Å and is not shorter than the other C–C distances (1.36–1.42 Å) in the C₈H₆ ring. It appears that the π system of the cyclooctatrienyne ligand is fully delocalized using the eight p orbitals for bonding with Zr1. The two sp^2 orbitals in the plane of the ring are used for bonding with Zr2. The distances C21–Zr2 and C22–Zr2 are equal to a normal σ Zr–C bond, which makes the bond order of C21–C22 closer to 2 than to 3. IR data support this since no $\nu(\text{C}\equiv\text{C})$ absorption (2250–2150 cm^{-1}) is observed. The C₈H₆ ring is slightly bent away (12.5 (6)°) from the zirconacyclopentane plane. The angle CE–(C₈H₆)–Zr1–CE(Cp*1) is 163.6 (5)°, close to the corresponding value (173.8°) in $\text{Cp}^*\text{ZrCOT}^{16}$ and indicates that this part of the molecule can be considered as a regular sandwich complex. The distortion is away from the other eight-membered ring in the dinuclear complex and is most probably due to steric congestion. The cyclooctatrienyne ligand is unknown as a free molecule. The smallest stable cycloalkyne known is cyclooctyne whereas cyclohexyne and even cycloheptyne are unstable as free ligands and can only be investigated by kinetic studies and trapping experiments.¹⁷ Coordinated to metals they can form stable complexes, of which many are known.¹⁸ Cyclooctyne complexes have been reported for Cu,¹⁹ Ag,²⁰ Ni,²¹ Pt,²² Mo,²³ W,²³ and Co.²⁴ Cyclooct-1-ene-3-yne is unstable but gives with cobalt the stable complex $(\text{C}_8\text{H}_{10})\text{Co}_2(\text{CO})_6$.²⁴ Also cycloocta-1,5-diene-3-yne as such is unknown but exists in $\text{CpMo}(\mu\text{-}\eta^6\text{:}\eta^2\text{-C}_8\text{H}_8)\text{MoCp}(\text{CO})_2$,²⁵ where it is bridging two molybdenum atoms. Octafluorocyclooctatetraene can lose two fluorine atoms to form hexafluorocyclooctatrienyne which can coordinate to metals.²⁶

The two Cp* ligands in $\text{Cp}^*\text{Zr}(\mu\text{-}\eta^3\text{:}\eta^2\text{-C}_8\text{H}_6)\text{ZrCp}^*(\eta^4\text{-C}_8\text{H}_8)$ show different metal ligand distances; thus, the mean bond distance to Zr1 is 0.06 Å shorter than to Zr2. The $\eta^4\text{-C}_8\text{H}_8$ ligand is bonded as a butadiene to Zr2; the uncoordinated part of the ligand is tilted out of the plane of the four bonded carbon atoms, and away from the metal. When the zirconium centers are considered neutral, both are trivalent and an electron count gives for Zr1 a 17- and for Zr2 a 15-electron system. The complex is thus expected to be paramagnetic, but this is clearly not the case. The long Zr1–Zr2 distance excludes a metal–metal bond, so that diamagnetism of the complex has to occur in a

(15) (a) McClain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* 1979, 101, 263. (b) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* 1979, 18, 1697.

(16) Rogers, R. D.; Teuben, J. H. *J. Organomet. Chem.* 1989, 359, 41.

(17) (a) Kreps, A. *Chemistry of Acetylenes*; Viehe, H. G. Ed.; M. Dekker: New York, 1969; Chapter 15. (b) Kreps, A.; Kimling, H. *Angew. Chem., Int. Ed. Engl.* 1971, 10, 509.

(18) (a) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* 1988, 88, 1047. (b) Bennett, M. A.; Schwemlein, H. P. *Angew. Chem., Int. Ed. Engl.* 1989, 28, 1296. (c) Hunt, R. L.; Wilkinson, G. *Inorg. Chem.* 1965, 4, 1270. (d) Chatt, J.; Rowe, G. A.; Williams, A. A. *Proc. Chem. Soc. London* 1957, 208. (e) Greaves, E. O.; Lock, C. J. L.; Maitlis, P. M. *Can. J. Chem.* 1968, 46, 3879. (f) Bennett, M. A.; Robertson, G. B.; Whimp, P. O.; Yoshida, T. *J. Am. Chem. Soc.* 1971, 93, 3797. (g) Robertson, G. B.; Whimp, P. O. *J. Am. Chem. Soc.* 1975, 97, 1051.

(19) Wittig, G.; Fischer, S. *Chem. Ber.* 1972, 105, 3542.

(20) Wittig, G.; Dorsch, H. L. *Liebigs Ann. Chem.* 1968, 711, 46.

(21) Wittig, G.; Fritze, P. *Liebigs Ann. Chem.* 1968, 712, 79.

(22) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* 1978, 100, 1750.

(23) Bennett, M. A.; Boyd, I. W.; Robertson, G. B.; Wickramasinghe, W. A. *J. Organomet. Chem.* 1985, 290, 181.

(24) Petersen, H.; Meier, H. *Nouv. J. Chim.* 1980, 4, 687.

(25) Goddard, R.; Knox, S. A. R.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* 1976, 559.

(26) (a) Doig, S. J.; Hughes, R. P.; Patt, S. L.; Samkoff, D. E.; Smith, W. L. *J. Organomet. Chem.* 1983, 250, C1. (b) Doig, S. J.; Hughes, R. P.; Davis, R. E.; Gadol, S. M.; Holland, K. D. *Organometallics* 1984, 3, 1921.

(10) Hunter, W. E.; Hrcncir, D. C.; Bynum, R. V.; Penttilä, R. A.; Atwood, J. L. *Organometallics* 1983, 2, 750.

(11) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* 1986, 108, 7411.

(12) Buchwald, S. L.; Lum, R. T.; Dewan, J. C. *J. Am. Chem. Soc.* 1986, 108, 7441.

(13) Arnold, J.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *Organometallics* 1989, 8, 415.

(14) Bennett, M. A.; Hambley, T. W.; Roberts, N. K.; Robertson, G. B. *Organometallics* 1985, 4, 1992.

different way. A possible explanation is electron transfer from Zr1 to Zr2 changing the oxidation states of Zr1 and Zr2 into four and two, respectively, thus forming a zwitterionic complex with a bridging cyclooctatrienylene ligand connecting the cationic $[\text{Cp}^*\text{Zr}(\eta^8\text{-C}_8\text{H}_8)]^+$ and the anionic $[\text{Cp}^*\text{Zr}(\eta^4\text{-C}_8\text{H}_8)\text{R}_2]^-$. The different oxidation states of the metal centers are reflected in the Cp*-Zr distances; the longer distance is associated with divalent Zr2.

With the structure of the dimer determined crystallographically, the NMR spectra can be interpreted completely (cf. Experimental Section). Although the dimer is insoluble in benzene or toluene, it is soluble in pyridine- d_5 and the ^1H spectrum in this solvent shows resonances of the Cp* ligands at $\delta = 1.89$ and 1.28 ppm. Signals of the cyclooctatrienylene ligand are located at $\delta = 6.94$ (d), 6.58 (dt), and 6.32 (dd) ppm and there is one resonance for the $\eta^4\text{-C}_8\text{H}_8$ ligand at $\delta = 5.93$ ppm, suggesting that in solution this ring is rapidly rotating. The ^{13}C NMR spectrum shows a resonance at $\delta = 179.66$ ppm (singlet in the ^1H coupled spectrum), assigned to the carbon atoms of the coordinated $\text{C}\equiv\text{C}$ bond, and four resonances at $\delta = 100\text{--}90$ ppm, where normally the resonances of C_8H_8 ligands are found. The IR spectrum shows an absorption at 1535 cm^{-1} , which suggests an uncoordinated $\text{C}=\text{C}$ bond and strong absorptions at 773 and 685 cm^{-1} , which lie in the region where absorptions for C_8H_8 ligands are usually found.

Synthesis and Characterization of FvZrCOT. FvZrCOT is the main product of the thermolysis of $\text{Cp}^*\text{Zr}(\text{COT})\text{CH}_2\text{Ph}$ in benzene at 110°C . It also can be made by thermal rearrangement of the dinuclear complex $\text{Cp}^*\text{Zr}(\mu\text{-}\eta^8\text{-}\eta^2\text{-C}_8\text{H}_8)\text{ZrCp}^*(\eta^4\text{-C}_8\text{H}_8)$ at about $170\text{--}200^\circ\text{C}$. The most convenient synthesis is by heating a solution of $\text{Cp}^*\text{Zr}(\text{COT})\text{CH}_2\text{SiMe}_3$ in benzene in an autoclave at 180°C for 24 h.

The ^1H NMR spectrum of FvZrCOT shows one signal for the methylene protons of the fulvene ligand at $\delta = 2.09$ ppm, which indicates a mirror plane through the molecule. Other fulvene complexes, for example Cp^*FvHf^6 and $\text{Cp}^*\text{FvTiCl}_2$,²⁷ appear to have diastereotopic methylene protons and give an AB pattern. The ^{13}C NMR resonance of the methylene carbon is found at $\delta = 41.77$ ppm, at rather high field compared to most reported fulvene zirconium compounds,^{1c} which are found between $\delta = 56$ and $\delta = 83$ ppm. The $^1J_{\text{CH}}$ value of the methylene carbon (146 Hz) is comparable with other FvZr complexes, indicating that the hybridization of the methylene carbon atom is between sp^2 ($^1J_{\text{CH}} \sim 160$ Hz) and sp^3 ($^1J_{\text{CH}} \sim 125$ Hz). The ^1H and ^{13}C NMR resonances of the cyclooctatetraene ligand are at normal positions ($\delta = 5.95$ and 94.72 ppm, respectively) compared with other ZrCOT compounds.²⁸ The IR spectrum shows absorptions at 2720 , 1475 , 1425 , 1380 , 1355 , 1155 , 1075 , 1020 , and 895 cm^{-1} , which can be ascribed to the Fv ligand, and the characteristic absorption of a regular $\eta^8\text{-cyclooctatetraene}$ ligand at 730 cm^{-1} . The olefinic C-H vibration of the fulvene methylene group is observed as a shoulder at 3040 cm^{-1} on the ν_{CH} absorption of the cyclooctatetraene ligand.

Fulvene ligands are known to coordinate in various ways and η^2 , η^4 , and η^6 coordination modes have been repor-

ted.^{1d,5,6,29} For FvZrCOT, η^6 -coordination is the most probable, leading to an 18-electron system. Whether this is realized through coordination of a planar fulvene ligand or through a bent, η^1 -methylene- η^5 -cyclopentadienyl type fulvene ligand is impossible to say. However, NMR data of group 4 metal fulvenes indicate that going from titanium to hafnium the latter becomes more important. This implies that FvZrCOT can most probably be considered as a "tucked in" analogue of compounds $\text{Cp}^*\text{Zr}(\text{COT})\text{R}$.

Concluding Remarks. Thermolysis of compounds $\text{Cp}^*\text{Zr}(\text{COT})\text{R}$ strongly depends on the nature of R. For $\text{R} = \text{Me}$ and CH_2SiMe_3 , the kinetic product is $\text{Cp}^*\text{Zr}(\mu\text{-}\eta^8\text{-}\eta^2\text{-C}_8\text{H}_8)\text{ZrCp}^*(\eta^4\text{-C}_8\text{H}_8)$, in which a cyclooctatrienylene ligand, formed by abstraction of two adjacent hydrogen atoms from a cyclooctatetraene ligand, bridges two zirconium centers. This dinuclear complex is thermally converted into the more thermodynamically stable fulvene compound FvZrCOT. The thermal decomposition of $\text{Cp}^*\text{Zr}(\text{COT})\text{CH}_2\text{Ph}$ gives the fulvene complex FvZrCOT preferentially at low temperatures, possibly through a different route. At higher temperatures formation of the dinuclear compound $\text{Cp}^*\text{Zr}(\mu\text{-}\eta^8\text{-}\eta^2\text{-C}_8\text{H}_8)\text{ZrCp}^*(\eta^4\text{-C}_8\text{H}_8)$ becomes more important.

Experimental Section

General Considerations. All compounds are extremely air sensitive, and manipulations were performed under nitrogen using Schlenk glassware, glovebox (Braun MB-200), or vacuum line techniques. Solvents (benzene, THF, ether, pentane) were purified by distillation from Na-K alloy. Mesitylene was distilled from Na. Pyridine and pyridine- d_5 were dried over molecular sieves (4 Å). Compounds $\text{Cp}^*\text{Zr}(\text{COT})\text{Cl}$, $\text{Cp}^*\text{Zr}(\text{COT})\text{Me}$ and $\text{Cp}^*\text{Zr}(\text{COT})\text{CH}_2\text{Ph}$ were prepared according to Spencer et al.²⁸ For $\text{Cp}^*\text{Zr}(\text{COT})\text{Cl}$ a more convenient procedure was developed (vide infra). NMR spectra were recorded in sealed tubes using a Varian VXR-300 or Bruker WH-90-DS spectrometer. The chemical shifts are reported relative to TMS, and the residual protons in the solvents were used as references (^1H NMR, δ (benzene- d_6) = 7.16 ppm, δ (THF- d_6) = 3.57 ppm, δ (cyclohexane- d_{12}) = 1.37 ppm, δ (pyridine- d_5) (o-proton) = 8.59 ppm; ^{13}C NMR, δ (benzene- d_6) = 127.96 ppm, δ (pyridine- d_5) (α -carbon) = 149.9 ppm). IR spectra were recorded from 4000 to 400 cm^{-1} on a Pye Unicam SP3-300 spectrophotometer. Samples were milled in Nujol and recorded between KBr disks. Elemental analyses were carried out at the Microanalytical Department of this Laboratory. Each value given is the average of at least two independent determinations.

Synthesis of $\text{Cp}^*\text{Zr}(\text{COT})\text{Cl}$. $\text{ZrCl}_4 \cdot 2\text{THF}$ was obtained by adding 10 mL of THF to a slurry of 8.12 g (34.8 mmol) of ZrCl_4 in 40 mL of pentane at 0°C . The viscous white suspension was dried in vacuo. The residue was dissolved in 80 mL of THF and treated with 70 mL of 0.50 M $\text{K}_2\text{C}_8\text{H}_8$ in THF (35 mmol), after which the solution was refluxed for 5 h. The solution became turbid, and the color changed to orange. Addition of 5.00 g (35.2 mmol) of Cp^*Li and refluxing overnight gave a yellow solution containing a gray precipitate. The solvent was removed in vacuum, and the yellow residue was extracted with 150 mL of benzene. Concentration to 40 mL at 70°C , followed by cooling to room temperature and addition of 80 mL pentane, gave 7.65 g (21 mmol, 60%) of $\text{Cp}^*\text{Zr}(\text{COT})\text{Cl}$.

(27) Pattiasina, J. W.; Agricola, F. T.; Meetsma, A.; Teuben, J. H.; Smeets, W. J. J.; Spek, A. L. Manuscript in preparation.

(28) Highcock, W. J.; Mills, R. M.; Spencer, J. L.; Woodward, P. J. *Chem. Soc., Dalton Trans.* 1986, 821.

(29) (a) Werner, H.; Crisp, G. T.; Jolly, P. W.; Kraus, H.-J.; Krüger, C. *Organometallics* 1983, 2, 1369. (b) Edelmann, F.; Behrens, U. *J. Organomet. Chem.* 1977, 128, 131. (c) Christofides, A.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Organomet. Chem.* 1982, 232, 279. (d) Weiss, E.; Hübel, W. *Chem. Ber.* 1962, 95, 1186. (e) Edelmann, F.; Lubke, B.; Behrens, U. *Chem. Ber.* 1982, 115, 1325. (f) Behrens, U. *J. Organomet. Chem.* 1976, 107, 103. (g) Bandy, J. A.; Mtetwa, V. S. B.; Prout, K.; Green, J. C.; Davies, C. E.; Green, M. L. H.; Hazel, N. J.; Izquierdo, A.; Martin-Polo, J. J. *J. Chem. Soc., Dalton Trans.* 1985, 2037. (h) Edelmann, F. Thesis, University of Hamburg, Federal Republic of Germany, 1983.

Synthesis of $\text{Cp}^*\text{Zr}(\text{COT})\text{CH}_2\text{SiMe}_3$. A mixture of 2.49 g (6.8 mmol) of $\text{Cp}^*\text{Zr}(\text{COT})\text{Cl}$ and 0.64 g (6.8 mmol) of $\text{LiCH}_2\text{SiMe}_3$ in 100 mL of pentane was stirred at room temperature for 16 h. After filtration, the orange solution was concentrated and cooled to -80°C . Isolation of the yellow-orange crystals and concentration and cooling of the mother liquor gave in total 2.13 g (5.1 mmol, 75%) of $\text{Cp}^*\text{Zr}(\text{COT})\text{CH}_2\text{SiMe}_3$. Anal. Calcd for $\text{C}_{22}\text{H}_{34}\text{SiZr}$: C, 63.24; H, 8.20; Zr, 21.83. Found: C, 62.96; H, 8.22; Zr, 21.82. IR (cm^{-1}): 3000 (w), 2940 (m), 2900 (m), 2865 (m), 2720 (w), 1490 (w), 1460 (m), 1440 (m), 1375 (s), 1345 (w), 1265 (w), 1245 (s), 1235 (s), 1015 (m), 915 (s), 895 (sh), 885 (s), 845 (s), 815 (s), 800 (sh), 770 (w), 735 (s), 725 (sh), 670 (m), 540 (m). ^1H NMR (benzene- d_6 /TMS, 300 MHz) (δ): 5.86 (s, 8 H, COT); 1.55 (s, 15 H, Cp^*); 0.34 (s, 9 H, CH_2SiMe_3); -0.50 (s, 2 H, CH_2SiMe_3). ^{13}C NMR (benzene- d_6 , 75.4 MHz) (δ): 117.40 (s, C_5Me_5); 94.86 (d, $^1J_{\text{CH}} = 162\text{ Hz}$, COT); 22.52 (t, $^1J_{\text{CH}} = 108\text{ Hz}$, CH_2SiMe_3); 12.22 (q, $^1J_{\text{CH}} = 126\text{ Hz}$, C_5Me_5); 5.38 (q, $^1J_{\text{CH}} = 117\text{ Hz}$, CH_2SiMe_3).

Thermolysis of $\text{Cp}^*\text{Zr}(\text{COT})\text{CH}_2\text{SiMe}_3$ in Benzene- d_6 . A sealed NMR tube containing a solution of 34 mg (0.077 mmol) of $\text{Cp}^*\text{Zr}(\text{COT})\text{CH}_2\text{SiMe}_3$ in 0.4 mL of benzene- d_6 was heated at 170°C . ^1H NMR spectra (22°C) were recorded at 2-h intervals during the first 10 h and then every 10 h. Formation of Me_4Si ($\delta = 0.00\text{ ppm}$) was complete after about 6 h, and the amount of insoluble $\text{Cp}^*\text{Zr}(\mu\text{-}\eta^5\text{-}\eta^2\text{-C}_5\text{H}_5)_2\text{ZrCp}^*(\eta^4\text{-C}_8\text{H}_8)$ appeared at a maximum while some FvZrCOT had been formed. On further heating, the precipitate dissolved and the intensity of the signals of FvZrCOT increased. The thermolysis was stopped after 30 h when no further changes were observed. Thermolyses of $\text{Cp}^*\text{Zr}(\text{COT})\text{CH}_2\text{SiMe}_3$ in THF- d_8 and cyclohexane- d_{12} were performed in the same way, showing the same overall features.

Thermolysis of $\text{Cp}^*\text{Zr}(\mu\text{-}\eta^5\text{-}\eta^2\text{-C}_5\text{H}_5)_2\text{ZrCp}^*(\eta^4\text{-C}_8\text{H}_8)$ in Benzene- d_6 . A sealed NMR tube containing 30 mg of $\text{Cp}^*\text{Zr}(\mu\text{-}\eta^5\text{-}\eta^2\text{-C}_5\text{H}_5)_2\text{ZrCp}^*(\eta^4\text{-C}_8\text{H}_8)$ in 0.4 mL of benzene- d_6 was kept at 170°C until no crystalline material was left (86 h). The ^1H NMR spectrum showed the presence of FvZrCOT , which accounted for about 85% of the total integrated intensity. In addition to the resonances of FvZrCOT , numerous overlapping signals are found around $\delta = 2.5\text{--}1.2\text{ ppm}$, accounting for about 15% of the total proton intensity. Assignment of this part of the ^1H NMR spectrum was not attempted.

Thermolysis of $\text{Cp}^*\text{Zr}(\text{COT})\text{Me}$ in Benzene- d_6 . A sealed NMR tube containing a solution of 40 mg (0.11 mmol) of $\text{Cp}^*\text{Zr}(\text{COT})\text{Me}$ in 0.4 mL of benzene- d_6 was kept at 170°C . The thermolysis was monitored at intervals as specified above for $\text{Cp}^*\text{Zr}(\text{COT})\text{CH}_2\text{SiMe}_3$. The thermolysis was stopped when all crystalline material was dissolved. ^1H NMR spectroscopy showed the formation of FvZrCOT in 60% yield.

Thermolysis of $\text{Cp}^*\text{Zr}(\text{COT})\text{CH}_2\text{Ph}$ in Benzene- d_6 . A solution of 136.0 mg (0.32 mmol) of $\text{Cp}^*\text{Zr}(\text{COT})\text{CH}_2\text{Ph}$ in 1.62 mL of benzene- d_6 was divided over three NMR tubes. After being sealed, the tubes were kept at 60, 85, and 110°C , respectively, until no starting material was left. In each case the solution became red with red-brown crystalline material. IR spectroscopy showed that the crystalline material was $\text{Cp}^*\text{Zr}(\mu\text{-}\eta^5\text{-}\eta^2\text{-C}_5\text{H}_5)_2\text{ZrCp}^*(\eta^4\text{-C}_8\text{H}_8)$. The ^1H NMR spectrum showed FvZrCOT present. From the ratio of the phenyl signal of $\text{Cp}^*\text{Zr}(\text{COT})\text{CH}_2\text{Ph}$ and the C_8H_8 signal of FvZrCOT the yield of the latter was determined (60°C , 74%; 85°C , 66%; 110°C , 53%). About 3% of the integrated intensity was assigned to an unidentified byproduct.

Synthesis of $\text{Cp}^*\text{Zr}(\mu\text{-}\eta^5\text{-}\eta^2\text{-C}_5\text{H}_5)_2\text{ZrCp}^*(\eta^4\text{-C}_8\text{H}_8)$. A sealed ampule containing 5.67 g (13.6 mmol) of $\text{Cp}^*\text{Zr}(\text{COT})\text{CH}_2\text{SiMe}_3$ in 20 mL of mesitylene was kept at 190°C for 6 h. From the solution dark red-brown crystals separated, which were filtered out and washed with pentane. Yield: 3.63 g (5.5 mmol, 81%) of $\text{Cp}^*\text{Zr}(\mu\text{-}\eta^5\text{-}\eta^2\text{-C}_5\text{H}_5)_2\text{ZrCp}^*(\eta^4\text{-C}_8\text{H}_8)$. Anal. Calcd for $\text{C}_{36}\text{H}_{44}\text{Zr}_2$: C, 65.60; H, 6.73; Zr, 27.68. Found: C, 65.51; H, 6.70; Zr, 27.80. IR (cm^{-1}): 3010 (m), 2975 (m), 2940 (sh), 2895 (m), 2720 (w), 1535 (s), 1475 (m), 1445 (m), 1415 (m), 1395 (sh), 1375 (m), 1360 (m), 1320 (w), 1205 (w), 1170 (w), 1150 (w), 1140 (m), 1055 (w), 1025 (m), 955 (w), 920 (w), 890 (w), 880 (m), 855 (w), 820 (sh), 810 (m), 780 (sh), 770 (s), 690 (s). ^1H NMR (pyridine- d_5 /TMS,

Table II. Crystal Data and Details of the Structure Determination of $\text{Cp}^*\text{Zr}(\mu\text{-}\eta^5\text{-}\eta^2\text{-C}_5\text{H}_5)_2\text{ZrCp}^*(\eta^4\text{-C}_8\text{H}_8)$

chem formula	$\text{C}_{36}\text{H}_{44}\text{Zr}_2$
mol wt	659.18
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	8.324 (2)
b, Å	15.966 (3)
c, Å	22.647 (3)
β , deg	92.56 (1)
V, Å ³	3007 (1)
Z	4
D_{calc} , g·cm ⁻³	1.456
$F(000)$, electrons	1360
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	7.0
cryst size, mm	$0.28 \times 0.21 \times 0.075$
temp, K	130
θ range, deg: min, max	1.28, 26.0
$\omega/2\theta$ scan, deg	$\Delta\omega = 0.70 + 0.35 \tan \theta$
data set	$h, 0 \rightarrow 10; k, -1 \rightarrow 19, l, -27 \rightarrow 27$
no. of data colld	7045
no. of unique data	5897
no. of rflns obsd ($I \geq 2.5\sigma(I)$)	4369
no. of refined params	355
final agreement factors	
$R_F = \sum(F_o - F_c)/\sum F_o $	0.085
$R_w = [\sum(w(F_o - F_c)^2)/\sum w F_o ^2]^{1/2}$	0.084
weighting scheme	$1/\sigma^2(F)$
min and max resid electron densities in final diff Fourier map, e/Å ³	-1.9, 1.8
max (shift/ σ) final cycle	0.231
av (shift/ σ) final cycle	0.002

300 MHz) (δ): 6.94 (d, $^3J_{\text{HH}} = 8.8\text{ Hz}$, 2 H, C_8H_8); 6.58 (dt, $^3J_{\text{HH}} = 8.8\text{ Hz}$, $^4J_{\text{HH}} = 4.0\text{ Hz}$, 2 H, C_8H_8); 6.32 (dd, $^3J_{\text{HH}} = 8.8\text{ Hz}$, $^4J_{\text{HH}} = 4.0\text{ Hz}$, 2 H, C_8H_8); 5.93 (s, 8 H, C_5H_5); 1.89 (s, 15 H, $\text{C}_5(\text{CH}_3)_5$); 1.28 (s, 15 H, $\text{C}_5(\text{CH}_3)_5$). ^{13}C NMR (pyridine- d_5 , 75.4 MHz) (δ): 179.66 (s, C_8H_8); 117.81 (s, $\text{C}_5(\text{CH}_3)_5$); 116.57 (s, $\text{C}_5(\text{CH}_3)_5$); 100.81 (d, $^1J_{\text{CH}} = 165\text{ Hz}$, C_8H_8); 99.74 (d, $^1J_{\text{CH}} = 149\text{ Hz}$, C_8H_8); 97.22 (d, $^1J_{\text{CH}} = 163\text{ Hz}$, C_8H_8); 95.10 (d, $^1J_{\text{CH}} = 170\text{ Hz}$, C_8H_8); 11.19 (q, $^1J_{\text{CH}} = 126\text{ Hz}$, $\text{C}_5(\text{CH}_3)_5$); 10.93 (q, $^1J_{\text{CH}} = 127\text{ Hz}$, $\text{C}_5(\text{CH}_3)_5$).

Synthesis of FvZrCOT . A solution of 5.18 g (12.5 mmol) of $\text{Cp}^*\text{Zr}(\text{COT})\text{CH}_2\text{SiMe}_3$ in 120 mL of benzene was placed in an autoclave and kept at 180°C for 24 hours. After cooling, the dark red-brown solution was transferred into a Schlenk flask and the solvent was removed in vacuo. The residue was washed three times with 75 mL of cold pentane (-20°C) and then dissolved in 60 mL of benzene. Concentrating the solution at 40°C to ca. 20 mL and condensing 100 mL of pentane onto the solution, followed by diffusion, gave dark-red crystals. Isolation and further crystallisation of the mother liquor gave a total of 2.81 g (8.5 mmol, 67%) of FvZrCOT . The compound was purified by sublimation (0.01 mmHg, 150°C). Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{Zr}$: C, 65.60; H, 6.73; Zr, 27.68. Found: C, 65.18; H, 6.78; Zr, 27.51. IR (cm^{-1}): 3040 (sh), 3035 (w), 2720 (w), 1475 (sh), 1425 (sh), 1380 (sh), 1360 (m), 1305 (w), 1175 (vw), 1155 (m), 1080 (w), 1025 (m), 910 (m), 900 (m), 860 (vw), 835 (m), 805 (sh), 780 (m), 755 (m), 730 (s), 670 (vw), 635 (w), 615 (m), 565 (vw), 505 (m). ^1H NMR (benzene- d_6 /TMS, 300 MHz) (δ): 5.95 (s, 8 H, COT); 2.09 (s, 2 H, $\text{C}_5(\text{CH}_3)_4\text{CH}_2$); 1.52 (s, 6 H, $\text{C}_5(\text{CH}_3)_4\text{CH}_2$); 1.11 (s, 6 H, $\text{C}_5(\text{CH}_3)_4\text{CH}_2$). ^{13}C NMR (benzene- d_6 , 75.4 MHz) (δ): 125.72, 122.74, and 122.44 (s, $\text{C}_5(\text{CH}_3)_4\text{CH}_2$); 94.72 (d, $^1J_{\text{CH}} = 166\text{ Hz}$, COT); 41.77 (t, $^1J_{\text{CH}} = 146\text{ Hz}$, $\text{C}_5(\text{CH}_3)_4\text{CH}_2$); 11.80 (q, $^1J_{\text{CH}} = 127\text{ Hz}$, $\text{C}_5(\text{CH}_3)_4\text{CH}_2$); 10.34 (q, $^1J_{\text{CH}} = 126\text{ Hz}$, $\text{C}_5(\text{CH}_3)_4\text{CH}_2$).

X-ray Diffraction: Molecular Structure of $\text{Cp}^*\text{Zr}(\mu\text{-}\eta^5\text{-}\eta^2\text{-C}_5\text{H}_5)_2\text{ZrCp}^*(\eta^4\text{-C}_8\text{H}_8)$. Crystals used for this study were grown from pyridine, glued on the top of a glass fiber, and transferred into the cold nitrogen stream of the low-temperature unit mounted on an Enraf-Nonius CAD-4F diffractometer interfaced to a PDP-11/23 computer. Unit cell dimensions and their standard deviations were determined from the setting angles of 20 reflections in the range $6.62^\circ < \theta < 17.52^\circ$. The monoclinic unit cell was checked for the presence of higher lattice symmetry.³⁰

The space group was derived from the observed systematic absences. Three standard reflections were monitored at regular intervals (3 h) and remained constant throughout the measurements. A 360° ψ -scan for a reflection close to axial (221) showed a variation in intensity up to 6% around the mean value. The net intensities of the data were corrected for the scale variation, Lorentz and polarization effects, and absorption (Gaussian integration method,³¹ grid 10 × 10 × 6; minimum and maximum correction, 1.054 and 1.171). Variance $\sigma^2(I)$ was calculated on the basis of counting statistics and the term (P^2/I) , where P (=0.028) is the instability constant as derived from the excess variance in the reference reflections.³² Equivalent reflections were averaged, resulting in 4369 reflections satisfying the $I \geq 2.5\sigma(I)$ criterion of observability.

The structure was solved by Patterson methods and subsequent partial structure expansion (SHELXS-86³³) and completed by Fourier techniques. The difference Fourier map indicated ring disorder in Cp* as well as in the COT rings. Rigid body refinements using idealized Cp* ring geometry (C–C = 1.42, C–C(Me) = 1.52 Å) and site occupancy factors were applied. However the refinements of these models and site occupancy factors did not converge. High thermal motion (but not resolvable disorder) was observed for the methyl groups. Attempts to find a satisfactory disorder model failed. One significant peak in the difference Fourier map located in the C29–C36 ring was set to C37 for a disordered position of C32. No hydrogen atom position could be located. The hydrogen atoms in the Cp* and COT ligands were included with their positions calculated by using sp² or sp³ hybridization at the C atom as appropriate and a fixed C–H distance of 1.0 Å. In a preliminary refinement cycle the hydrogen atoms of the methyl groups were allowed to rotate about the C–C axis. Hydrogen atoms were included in the final refinement cycles riding on their carrier atom with one common isotropic thermal parameter and used in the structure factor calculations but not refined. The hydrogen atoms on carbon atoms C32 and C37 were included with the sof's (sof = site occupation factor) of their carrier atom. Weights were introduced in the final refinement cycles. This led to a final refinement on F by block-diagonal least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms and one common isotropic temperature factor for the hydrogen atoms which converged at $R_F = 0.085$ ($R_w = 0.084$). The quantity minimized by the least-squares procedure was: $Q = \sum_h [w(|F_o| - |F_c|)^2]$. The temperature factors of C37 were nonpositive definite and some atoms showed unrealistic temperature factors, suggesting some degree of disorder. The 15 peaks that are greater than 1 e/Å³ on the final difference-Fourier map are within 1 Å distance of the Zr or the C atoms. This fact suggests the major disorder problem with the structure is related to the orientation of the whole complex in the lattice rather than the local disorder of the Cp* rings.³⁴ The crystal exhibited some secondary extinctions for which the F values were corrected by refinement of an empirical isotropic extinction parameter³⁵ ($g = 0.49$ (8) × 10⁻⁴). Two reflections with $w(|F_o| - |F_c|) > 10$ were excluded from the final refinement cycle. Crystal data and experimental details of the structure determination are compiled in Table II. Final fractional

Table III. Final Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Non-H Atoms, with Esd's in Parentheses

	x	y	z	$U_{eq}, \text{\AA}^2$ ^a
Zr1	0.8767 (1)	0.10432 (6)	0.28927 (4)	0.0422 (3)
Zr2	1.0932 (1)	0.18421 (5)	0.13536 (3)	0.0214 (2)
C1	0.901 (2)	0.2212 (8)	0.3604 (5)	0.111 (6)
C2	0.951 (1)	0.1536 (8)	0.3899 (5)	0.082 (5)
C3	0.825 (1)	0.0978 (6)	0.3962 (3)	0.035 (3)
C4	0.6883 (9)	0.1322 (5)	0.3685 (3)	0.029 (3)
C5	0.740 (2)	0.2113 (6)	0.3463 (3)	0.069 (5)
C6	0.994 (3)	0.2995 (9)	0.3504 (6)	0.30 (2)
C7	1.119 (1)	0.143 (1)	0.4163 (7)	0.20 (1)
C8	0.838 (2)	0.0189 (7)	0.4293 (4)	0.095 (6)
C9	0.524 (1)	0.0983 (9)	0.3699 (5)	0.088 (6)
C10	0.631 (3)	0.2725 (9)	0.3163 (5)	0.23 (1)
C11	0.969 (1)	0.1096 (9)	0.0463 (5)	0.086 (6)
C12	1.082 (1)	0.1559 (7)	0.0250 (4)	0.060 (4)
C13	1.224 (1)	0.1305 (7)	0.0439 (4)	0.050 (3)
C14	1.207 (2)	0.0628 (7)	0.0793 (4)	0.085 (5)
C15	1.045 (2)	0.0464 (6)	0.0811 (4)	0.114 (7)
C16	0.797 (1)	0.106 (1)	0.0362 (7)	0.44 (3)
C17	1.033 (3)	0.214 (1)	-0.0199 (5)	0.42 (3)
C18	1.383 (2)	0.155 (1)	0.0230 (7)	0.23 (1)
C19	1.329 (3)	0.010 (1)	0.1092 (6)	0.44 (3)
C20	0.974 (3)	-0.0249 (9)	0.1068 (6)	0.45 (3)
C21	0.904 (1)	0.1277 (6)	0.1873 (3)	0.037 (3)
C22	1.052 (1)	0.0988 (5)	0.2097 (3)	0.023 (3)
C23	1.113 (1)	0.0419 (5)	0.2524 (4)	0.050 (4)
C24	1.025 (2)	-0.0197 (6)	0.2837 (5)	0.106 (7)
C25	0.861 (2)	-0.0435 (6)	0.2850 (5)	0.16 (1)
C26	0.718 (2)	-0.0124 (9)	0.2635 (7)	0.18 (1)
C27	0.664 (1)	0.052 (1)	0.2292 (6)	0.144 (8)
C28	0.738 (1)	0.1136 (9)	0.1958 (4)	0.081 (5)
C29	1.040 (1)	0.3113 (5)	0.1888 (4)	0.057 (4)
C30	1.190 (1)	0.2844 (6)	0.2083 (4)	0.055 (4)
C31	1.329 (1)	0.2629 (8)	0.1778 (6)	0.091 (5)
C32 ^b	1.394 (2)	0.3118 (7)	0.1136 (5)	0.050 (5)
C33	1.310 (1)	0.3615 (6)	0.0767 (4)	0.045 (3)
C34	1.153 (1)	0.3762 (7)	0.0672 (8)	0.110 (7)
C35	1.005 (2)	0.3607 (8)	0.0772 (6)	0.095 (6)
C36	0.974 (2)	0.3273 (6)	0.1313 (4)	0.097 (6)
C37 ^c	1.455 (4)	0.272 (2)	0.147 (1)	0.03 (1)

^a $U_{eq} = 1/3 \sum_i \sum_j U_{ij}(a_i^* a_j^*) a_i a_j$. ^b Indicates an sof of 0.71 (1); nonpositive definite temperature factors. ^c Indicates an sof of 0.29 (1).

atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table III. Molecular geometry data are collected in Table I. Tables of hydrogen atoms positions, thermal parameters, and comprehensive bond distances and angles are given as supplementary material for this paper. Scattering factors were taken from Cromer and Mann.³⁶ Anomalous dispersion factors³⁷ were included in F_c . All calculations were carried out on the CDC-Cyber 170/760 computer of the University of Groningen with the program packages XTAL³⁸ and EUCLID³⁹ (calculation of geometric data) and a locally modified version of the program PLUTO⁴⁰ (preparation of illustrations).

Supplementary Material Available: Tables of crystal data, anisotropic thermal parameters, atomic coordinates, bond lengths, bond angles, and torsion angles involving H atoms (17 pages). Ordering information is given on any current masthead page.

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(36) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *24*, 321.

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

(38) Hall, S. R.; Stewart, J. M. *XTAL2.2 Users Manual*; University of Western Australia, Perth, Australia, and University of Maryland, College Park, MD, 1987.

(39) Spek, A. L. The EUCLID package. In *Computational Crystallography*; Sayre, D., Ed.; Oxford University Press (Clarendon): London/New York, 1982; p 528.

(40) Meetsma, A. Extended version of the program PLUTO. University of Groningen, The Netherlands, 1986 (unpublished).

(31) Spek, A. L. *Proc. 8th Eur. Crystallogr. Meet.*; Liege, Belgium, 1983.

(32) McCandlish, L. E.; Stout, G. H.; Andrews, L. C. *Acta Crystallogr., Sect. A* **1975**, *31*, 245.

(33) Sheldrick, C. M. *SHELXS86, Program for crystal structure solution*; University of Göttingen: Göttingen, Federal Republic of Germany, 1986.

(34) In a preliminary experiment with a polyhedral sphere shaped single crystal and also at 130 K a unit cell was found with an a -axis of 24.97 Å (3 σ). The structure was solved with three independent molecules in the asymmetric unit. Refinement led to a final R value of 0.16. The molecules had the same configuration as described here. Afterward, a repeated experiment with the same type of crystal showed the same effect: at 130 K the reflections of the supercell were observed, and at room temperature they could not be observed by the diffractometer or on a Weissenberg film. In the described experiment in this paper a plate-shaped single crystal was selected and no super reflections were observed.

(35) Zachariasen, W. H. *Acta Crystallogr., Sect. A* **1967**, *23*, 558.