

Reductive Coupling of Fulvenes with Calcium for C_2 -Symmetric *ansa*-Metallocenes: Syntheses and Molecular Structures of *trans*- $\text{Ph}_2\text{C}_2\text{H}_2(\eta^5\text{-C}_5\text{H}_4)_2\text{Ca}(\text{THF})_2$ and *trans*- $\text{Ph}_2\text{C}_2\text{H}_2(\eta^5\text{-C}_5\text{H}_4)_2\text{ZrCl}_2$

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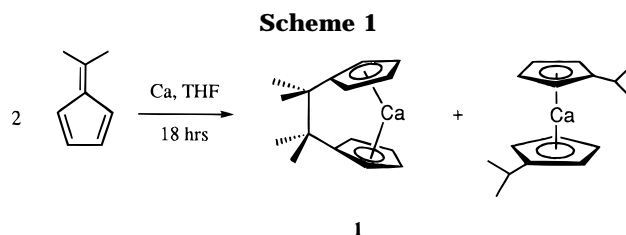
Received May 27, 1997[⊗]

Reductive coupling of dimethylfulvene with alkaline earth metals yields inseparable mixtures of the tetramethylethylene-bridged complex $\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{M}$ and the unbridged metallocene (*i*-PrCp)₂M (M = Mg, Ca, Sr, Ba). In contrast, the reductive coupling of phenylfulvene with activated calcium in THF gives nearly quantitative yields of a mixture of *cis*- and *trans*-diphenylethanediy-bridged *ansa*-calcocenes. The more soluble *cis* isomer can be removed by recrystallization, yielding the C_2 -symmetric *trans*- $\text{Ph}_2\text{C}_2\text{H}_2(\eta^5\text{-C}_5\text{H}_4)_2\text{Ca}(\text{THF})_2$ (*trans*-**2**). The molecular structure of this *ansa*-calcocene shows the cyclopentadienyl rings to be bound in an η^5 fashion to the calcium center. This versatile reagent gives high yields of C_2 -symmetric transition metal *ansa*-metallocene complexes *via* the facile reaction of *trans*-**2** with metal chlorides (e.g., FeCl_2 and ZrCl_4). The molecular structure of the corresponding *ansa*-zirconocene dichloride complex is described.

Introduction

The inclusion of interannular bridges between the cyclopentadienyl (Cp) rings of metallocenes yields the so-called *ansa*-metallocenes. An important consequence of the bridging moiety is the change in electronic behavior¹ of the metal center imparted by the restricted geometry of the Cp rings. One example of this change in electronic properties is the reactivity of the *ansa*-chromocenes reported by Brintzinger.² In sharp contrast to the unbridged Cp_2Cr ,^{3,4} the 18-electron tetramethylethylene-bridged chromocene carbonyl complex is stable and isolable.

We recently reported⁵ a facile route toward these *ansa*-chromocene complexes using the *ansa*-calcocene reagent reported by Edelmann's group, which is prepared by the reductive coupling of dimethylfulvene with activated calcium.⁶ Because of its ease of preparation and high solubility in tetrahydrofuran, this *ansa*-calcocene is a much better reagent for the preparation of *ansa*-chromocenes than the corresponding Grignard reagent used by Brintzinger.² Unfortunately, bis(iso-



propylcyclopentadienyl)calcium is a persistent impurity formed in the synthesis of the *ansa*-calcocene reagent. Our inability to eliminate this impurity prompted us to further investigate the nature of the coupling of fulvenes.

We report here the results of our initial studies into the reductive coupling of dimethylfulvene, along with the high-yield synthesis and complete characterization of a new, C_2 -symmetric *ansa*-calcocene from phenylfulvene. We also describe here its versatility as a reagent in the preparation of *ansa*-metallocenes and the molecular structure of a new *ansa*-zirconocene complex.

Results and Discussion

Reductive Coupling of Dimethylfulvene. As shown in Scheme 1, reaction of dimethylfulvene with activated calcium powder following Edelmann's method⁶ gives the tetramethylethylene-bridged calcocene **1**. In addition to the expected methyl resonances for **1**, the ¹H NMR spectrum (DMSO-*d*₆) of the isolated solid shows resonances at δ 1.10 (doublet, $J = 6.8$ Hz) and 2.75 (septet, $J = 6.8$ Hz) which we assign to the methyl and methine protons, respectively, of bis(isopropylcyclopentadienyl)calcium. Even when using identical reaction conditions, the amount of isopropyl impurity varies (15–45%). Attempts to remove (*i*-PrCp)₂Ca by recrystallization and sublimation were unsuccessful.

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[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1997.

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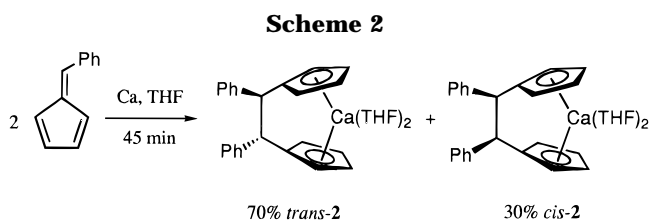
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Although not reported by Edlmann and co-workers in their alkaline earth and lanthanide metal coupling studies,^{6–8} the isopropylcyclopentadienyl impurity has been observed by others in the preparation of *ansa*-ferrocenes and -titanocenes from the sodium-promoted coupling of dimethylfulvene^{9–11} and by direct reaction of dimethylfulvene with iron vapor.¹² Schwemlein and Brintzinger suggested that over-reduction of dimethylfulvene by the metal results in a dianionic intermediate that abstracts a proton from dimethylfulvene. They prescribed using metals with reduction potentials less than -2.0 V, and by using magnesium and CCl_4 , they successfully prepared the di-Grignard reagent free of impurities, albeit in low yields.¹³

With this in mind, we sought to preclude formation of $(i\text{-PrCp})_2\text{Ca}$ and shorten the reaction time by performing the reductive coupling of dimethylfulvene with Rieke calcium.^{14,15} The end result in all cases was the nearly exclusive formation of $(i\text{-PrCp})_2\text{Ca}$, indicating that the more reactive form of the calcium metal leads to more of the isopropyl-containing product. Similar reactions using Mg and Ba powders and Sr pellets all yielded mixtures of the *ansa* and unbridged alkaline earth metallocenes. Our observations of the isopropyl impurity for the series (Mg, Ca, Sr, and Ba) are consistent with those of Schwemlein and Brintzinger,¹³ but our data further suggest that the reduction potential of the metal does not determine the product formed.

Reductive Coupling of Phenylfulvene. Assuming that the $(i\text{-PrCp})_2\text{Ca}$ co-product arises from the facile removal of the methyl hydrogens from dimethylfulvene, we sought to avoid this problem by using a fulvene devoid of abstractable hydrogens. 6-Phenylfulvene fits this requirement very nicely.

Using Edlmann's method,⁶ the reductive coupling of phenylfulvene with activated calcium in THF was exothermic and *complete within 45 min*; in contrast, reaction with dimethylfulvene required 8–14 h (Scheme 2). Filtration of the mixture and removal of the solvent yielded a mixture of the *cis* and *trans* isomers (30:70) of the *ansa*-(1,2-diphenylethano)calcocene **2** (88–95%) as a microcrystalline, grayish solid that is soluble in THF and toluene (Scheme 2).

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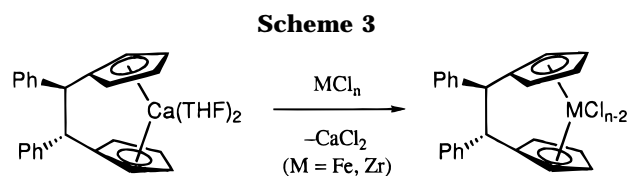
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The ^1H NMR spectrum of this solid in $\text{DMSO}-d_6$ shows the singlet resonances of the benzylic hydrogens of the *ansa* bridge at δ 4.97 and 4.66. Both isomers are predicted to have four Cp resonances and a single benzylic resonance, as the *trans* isomer is C_2 -symmetric and the *cis* isomer has a mirror plane bisecting the midpoint of the ethano bridge. In fact, Green and co-workers reported the reductive coupling of phenylfulvene with $(\eta\text{-C}_6\text{H}_6)\text{Fe}(\text{PMe}_3)_2$ but were unable to resolve the ^1H NMR resonances of the two isomers of the resultant [2]-ferrocenophane.¹⁶ Fortunately, *trans*-**2** could be purified readily by selective recrystallization, thereby permitting the unequivocal assignment of the peaks in the NMR spectrum, which shows three Cp resonances at 5.88, 5.56, and 5.35 (ratio 1:2:1) and the benzylic hydrogens at 4.66. Integrations of the resonances at δ 3.61 and 1.78 indicate the presence of two molecules of THF per calcocene, and this was confirmed by the elemental analysis. An X-ray diffraction analysis confirmed the *trans* geometry of the phenyl groups (see below).

We attribute the exclusive formation of **2** to two factors: (1) the absence of abstractable hydrogens, as in dimethylfulvene, and (2) the stabilizing influence of a phenyl group on the nascent benzylic radical formed in the first step of the reduction. The predominance of the C_2 -symmetric *trans* isomer in the product mixture suggests that the steric bulk of the phenyl group has a significant effect on the outcome of the coupling of phenylfulvene. Preliminary studies on the reductive coupling of other bulky aryl fulvenes supports this conclusion, and full details will appear in a subsequent report.

Reactivity of *ansa*-Calcocene 2. Scheme 3 shows the reaction of the *ansa*-calcocene with transition metals. In order to determine the versatility of *trans*-**2** in the preparation of transition metal *ansa*-complexes, we prepared a single isomer of the *ansa*-ferrocenes first reported by Green and co-workers.¹⁶ The reaction of FeCl_2 with a THF solution of the calcocene proceeded smoothly in approximately 4 h, giving the orange ferrocenophane, *trans*-**3**, in 92% yield. It is clear from the ^1H NMR spectrum (C_6D_6) of this product why unequivocal identification of a mixture of the two isomers is impossible. The single benzylic resonance of *trans*-**3** appears at δ 4.45 amongst four equally intense pseudo-triplet Cp–H resonances at 3.90, 4.24, 4.55, and 4.90. On the basis of the configuration of the calcocene precursor, we formulate this product as *trans*- $\text{Ph}_2\text{C}_2\text{H}_2(\eta^5\text{-C}_5\text{H}_4)_2\text{Fe}$.

Similarly, we were successful in preparing the *ansa*-zirconocene dichloride complex by reacting *trans*-**2** with ZrCl_4 in THF or toluene. Reaction times of under 6 h gave yields of *trans*-**4** in excess of 85%, and the product is soluble in THF, toluene, and chlorinated solvents. The ^1H NMR spectrum (C_6D_6) of the *ansa*-zirconocene

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Table 1. Crystallographic Data for *trans*-Ph₂C₂H₂(η⁵-C₅H₄)₂Ca(THF)₂ (2**) and *trans*-Ph₂C₂H₂(η⁵-C₅H₄)₂ZrCl₂ (**4**)**

empirical formula	C ₃₂ H ₃₆ O ₂ Ca	C ₂₅ H ₂₂ Cl ₄ Zr
fw	492.69	555.45
cryst syst	orthorhombic	monoclinic
space group	<i>Pbca</i>	<i>P2₁/c</i>
<i>a</i> , Å	14.3595(3)	12.3721(4)
<i>b</i> , Å	15.7747(1)	12.2086(4)
<i>c</i> , Å	23.8784(6)	16.1688(5)
α, deg	90	90
β, deg	90	94.636(1)
γ, deg	90	90
<i>V</i> , Å ³	5422.5(2)	2434.24(13)
<i>Z</i>	8	4
ρ (calcd), g cm ⁻³	1.207	1.516
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, cm ⁻¹	2.58	9.01
<i>T</i> , K	218	299
R1 ^a	0.1009	0.0589
wR2 ^b	0.2111	0.1613

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = [\sum (w_i(F_o^2 - F_c^2)^2) / \sum (w_i F_o^2)]^{1/2}.$$

Table 2. Selected Bond Distances and Angles

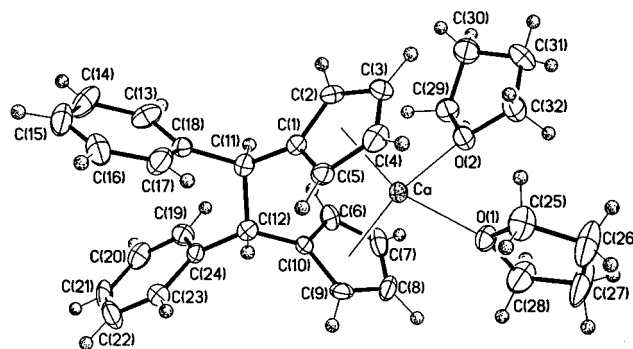
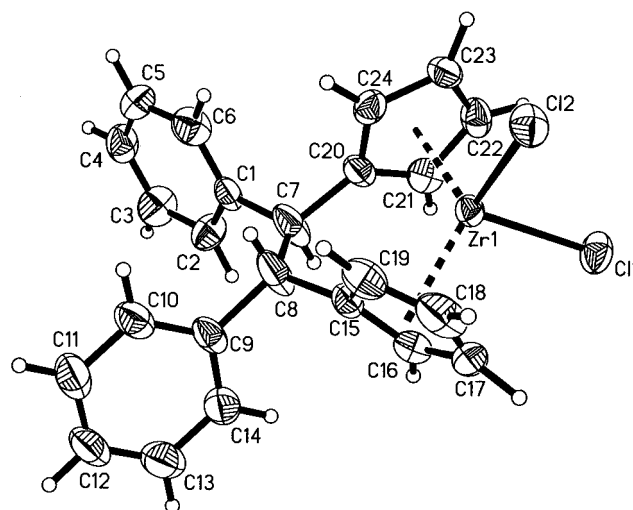
	<i>ansa</i> -Metalloocene	
	<i>trans</i> - 2 (M = Ca, L = OC ₄ H ₈)	<i>trans</i> - 4 (M = Zr, L = Cl)
Average Bond Distance (Å)		
M–L	2.36	2.44
M–Cp(centroid)	2.42	2.25
Bond Angle (deg)		
cent–M–cent	119.9	124.6
L–M–L	84.7	98.5
dihedral ^a	90.3	89.1
Cp–Cp	58.0	62.6

^a Dihedral angle at the intersection of the L–M–L and cent–M–cent planes; 90° is the expected angle.

showed resonances at δ 4.17 (singlet) for the benzylic hydrogens and δ 5.62, 5.67, 6.33, and 6.69 for the ring protons. The resonances for the Cp hydrogens of *trans*-**4** are shifted downfield and are not as widely separated as the signals for the ring protons of the corresponding ferrocenophane. The presence of only one isomer is supported by the single benzylic resonance in the ¹H and ¹³C NMR spectra. The *trans* configuration was confirmed by a single-crystal X-ray structure determination (see below).

Molecular Structure of *trans*-2**.** The molecular structures of *trans*-**2** and *trans*-**4** were determined by X-ray diffraction. Crystallographic data for both complexes are collected in Table 1, and selected bond distances and angles are presented in Table 2. Complete crystallographic details are available in the Supporting Information. Two molecules of THF are coordinated to the calcium in *trans*-**2**, and a disordered molecule of CH₂Cl₂ is found in the crystal lattice with *trans*-**4**. As can be seen in Figures 1 and 2, the phenyl groups on the ethano bridge are mutually *trans* and both metals are coordinated to the cyclopentadienyl rings in an η⁵ fashion. The M–Cp(centroid) distances are 2.411 Å (M = Ca) and 2.422 Å (M = Zr), and the torsion angles about the ethylene bridge (Ph_{ipso}–C–C–Ph_{ipso}) are 38.3° and 38.7°, respectively.

Figure 1 shows that the two THF molecules lie in the equatorial wedge of the *ansa*-calcocene, one of them perpendicular and the other coplanar to the wedge. The calcium atom is in a distorted tetrahedral environment, with angles of 84.7° for O1–Ca–O2 and 119.9° for cent–

**Figure 1.** Molecular structure of *ansa*-calcocene *trans*-**2** (ORTEP, 50% ellipsoids) showing atom numbering scheme.**Figure 2.** Molecular structure of *ansa*-zirconocene *trans*-**4** (ORTEP, 30% ellipsoids) showing atom numbering scheme.

Ca–cent. Although this angle compares favorably to the 119.0° angle observed in Edlmann's tetramethylethylene-bridged calcocene,⁶ it is small when compared to other unbridged, bent calcocenes. Without the constraint imposed by a bridge, cent–Ca–cent angles of 134–162° are commonly observed.^{17,18} For example, (C₅H₄Me)₂Ca·DME is reported to have a cent–Ca–cent angle of 134.8°,¹⁹ and (C₅Me₅)₂Ca has a cent–Ca–cent angle of 147.7°.²⁰ A space-filling model of *trans*-**2** revealed that considerable room remains for rotation of the THF molecules, and this may account for the ultimately poor resolution of the atoms.

The structure of the dichloromethane solvate of *trans*-**4** is similar to other *ansa*-zirconocene structures. The average Zr–Cl bond distance of 2.44 Å and the Cl–Zr–Cl bond angle of 98.5° are comparable to those observed in other *ansa*-zirconocene dichloride complexes.^{21,22} The cent–Zr–cent angle is 124.6°, and the dihedral angle at the intersection of the cent–Zr–cent and Cl–Zr–Cl planes is 89.1°. The two Cp rings of *trans*-**4** make an angle of 62.6°, again consistent with that reported for similar complexes.^{21,22}

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Conclusion

We have demonstrated a remarkably clean synthetic route toward *ansa*-calcocenes via the reductive coupling of phenylfulvenes. The isolation of the C_2 -symmetric *trans* isomer of (1,2-diphenylethano)caltocene as the major product can possibly be exploited for the development of optically pure, C_2 -symmetric *ansa*-metallocenes. Moreover, the high yields obtained for both the iron and zirconocene *ansa*-complexes has been observed for analogous *ansa*-chromocene complexes,²³ suggesting that the pre-eclipsed conformation of the bridged cyclopentadienyl rings discourages the oligomerization possible with lithium, sodium, and Grignard salts of *ansa* ligands. A mechanistic investigation into the nature of the reductive coupling of fulvenes is in progress.²⁸

Experimental Section

General. Dimethylfulvene²⁴ and phenylfulvene^{25,26} were prepared following the method described by Little and Stone.²⁴ Calcocene **2** was prepared according to the published method.⁶ THF and toluene were stored over and distilled from Na/benzophenone immediately prior to use. Methylene chloride was stored over CaH₂. Petroleum ether was stored over and distilled from the Cp₂TiCl₂-Zn adduct.²⁷ All other reagents were used as received. Air- and moisture-sensitive compounds were handled and stored in a nitrogen atmosphere drybox and were manipulated using argon and vacuum Schlenk techniques. NMR spectra were recorded on Bruker AC 200 or NR/300 MHz instruments and referenced to the proton impurity of the solvent (C₆D₆, 7.15; DMSO-*d*₆, 2.50; THF-*d*₆, 1.85). Infrared spectra were recorded using a Bio-Rad FTS spectrophotometer.

Reaction of Dimethylfulvene with Rieke Metals. The reaction of dimethylfulvene with activated calcium powder is similar to those reactions using Mg and Ba powders. Using Hanusa's method,¹⁵ CaI₂ (8.50 g, 28.9 mmol) was stirred in THF with freshly cut potassium (2.26 g, 57.8 mmol). The mixture was heated at reflux under argon for 8 h, and a grey powder formed as the potassium was consumed. The mixture was cooled to room temperature, a cool (10 °C) water bath was placed around the reaction flask, and dimethylfulvene (6.14 g, 58.0 mmol) was added dropwise to the rapidly stirred mixture. The yellow color of the fulvene dissipated almost immediately, and the reaction was complete within 30 min. Filtration of the mixture through a frit followed by evaporation of the solvent yielded a foamy, glassy solid. The ¹H NMR spectrum of this solid showed resonances for the methyl protons **1** at δ 1.38 (s), and resonances for the methyl and methine protons of the isopropyl species appeared at δ 1.10 (d, $J = 6.8$ Hz) and 2.75 (sept, $J = 6.8$ Hz).

Preparation of *trans*-(1,2-Diphenyl-1,2-dicyclopentadienyl)ethanediylcalcium Bis(tetrahydrofuran), *trans*-2**.** Calcium granules (2.0 g, 50 mmol) were activated as before in THF, and then solid phenylfulvene (7.71 g, 50 mmol) was added to the reaction flask under a flow of argon. An exothermic reaction ensued and was complete within 30 min, as evidenced by the disappearance of the orange color. The mixture was filtered through a medium frit, and the filtrate

was evaporated to dryness to yield a greyish powder that was washed twice with petroleum ether (crude yield 8.20 g, 93%). The solid was recrystallized from hot THF to yield clear colorless prisms that clouded over time (5.63 g). ¹H NMR (DMSO-*d*₆, δ): 1.78, 3.61 (m, 16H, THF), 4.66 (s, 2H, PhCHCp), 5.35, 5.56, 5.88 (1:2:1, pseudo t, 8H, C₅H₄), 6.80–7.80 (m, 10H, C₆H₅). ¹³C NMR (CDCl₃, δ): 25.1, 67.0 (THF), 54.0 (PhCHCp), 101.6, 103.5, 106.6, 107.5, 124.2 (C₅H₄), 127.3, 127.7, 128.2, 147.8 (C₆H₅). Principle IR absorptions (Nujol cm⁻¹): 3058 (m), 3022 (m), 1495 (w), 1488 (w), 1340 (vw), 1026 (s), 878 (m), 806 (m), 784 (m), 734 (s), 709 (s), 700 (s). Anal. Calcd (Found) C₃₂H₃₆O₂Ca: C, 78.02 (78.00); H 7.39 (7.36).

Preparation of *trans*-(1,2-Diphenyl-1,2-dicyclopentadienyl)ethanediyliron(II), *trans*-3**.** THF was added by vacuum transfer to a mixture of *trans*-**2** (0.28 g, 0.71 mmol) and FeCl₂ (0.09 g, 0.71 mmol). The mixture was warmed to room temperature and stirred for 6 h, during which time the mixture became orange. The solvent was removed, and the residue was extracted with toluene and filtered. The filtrate was evaporated and dried under vacuum for 4 h to give a microcrystalline orange solid weighing 0.25 g (92%). ¹H NMR (C₆D₆, δ): 4.45 (s, 2H, PhCHCp), 3.90, 4.24, 4.55, 4.90 (pseudo t, 8H, C₅H₄), 7.03 (m, 10H, C₆H₅). The spectrum is consistent with that reported for the inseparable mixture of *cis* and *trans* isomers.¹⁶

Preparation of *trans*-(1,2-Diphenyl-1,2-dicyclopentadienyl)ethanediylzirconium(IV) Dichloride, *trans*-4**.** THF was added by vacuum transfer to a mixture of *trans*-**2** (0.200 g, 0.405 mmol) and ZrCl₄ (0.094 g, 0.405 mmol). The mixture was warmed to room temperature and stirred for 6 h. The solvent was removed, and the residue was extracted with methylene chloride and filtered. The filtrate was evaporated and dried under vacuum for 2 h to give an off-white solid weighing 0.170 g (89%). ¹H NMR (C₆D₆, δ): 4.17 (s, 2H, PhCHCp), 5.63, 5.67, 6.33, 6.69 (pseudo t, 8H, C₅H₄), 6.86 (m, 10H, C₆H₅). ¹³C NMR (CDCl₃, δ): 54.3 (PhCHCp), 105.9, 113.2, 120.4, 127.3, 127.4 (C₅H₄), 127.7, 128.6, 135.4, 140.5 (C₆H₅). Similar yields were obtained using toluene, and the reaction mixture was filtered and the filtrate evaporated. Anal. Calcd (Found) for C₂₄H₂₀Cl₂Zr: C, 61.47 (61.10); H, 4.22 (4.30). Crystals suitable for X-ray analysis were obtained by recrystallization from methylene chloride/petroleum ether.

X-ray Structural Determinations. *trans*-**2**: Crystallographic data are collected in Table 1. A colorless crystal was found to belong to the orthorhombic space group *Pbca* from diffraction symmetry and systematic absences in the diffraction data. Data collection using the Siemens P4/CCD SMART system extended to $2\theta = 56^\circ$. An empirical correction for absorption was applied to the data. All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were included as idealized contributions. Whereas the esd's on the individual bond parameters are in a normal range, the overall *R* factor is higher than normal (ca. 10%) due to diffuseness in the diffraction arising from the presence of two closely spaced and ultimately unresolvable positions for the two bound THF molecules. In any given Ca complex, one of the THF molecules (containing O(1)) is parallel to the metallocene wedge plane and the other is more nearly perpendicular.

trans-**4**: Crystallographic data are listed in Table 1. The X-ray diffraction data for *trans*-**4** were collected on a Siemens SMART diffractometer equipped with a CCD detector. The frame data were acquired with the SMART software using a Siemens three-circle platform using Mo K α radiation ($\lambda = 0.71073$ Å) from a fine-focus tube. Cell constants were determined from 60 30-s frames. A complete hemisphere of data was scanned on omega (0.3°) with a run time of 10 s per frame at the detector resolution of 512 × 512 pixels. A total of 1271 frames were collected in three sets, and a final set of 50 frames, identical to the first 50 frames, were also collected to determine crystal decay. The structure was solved by direct methods using the SHELX-90 program and refined by least square methods on F^2 . All non-hydrogen atoms were refined

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anisotropically. The hydrogen atoms were located from the difference electron density maps and were included in the refinement process in an isotropic manner. None of the crystals used for the diffraction studies showed any decomposition during data collection.

All software used was contained in the SMART and SHELX-TL(5.2) libraries of programs (Siemens XRD, Madison, WI).

Acknowledgment. The authors would like to thank Dr. Richard Williams (University of Idaho) for helpful discussions and Mr. Robert Hubbard for assistance with

fulvene syntheses. We thank the National Science Foundation (Grant No. CHE-9502739) for financial support.

Supporting Information Available: Tables of crystallographic data, positional parameters, bond lengths and angles, thermal parameters, and atomic parameters of hydrogen atoms for *trans-2* and *trans-4* (13 pages). Ordering information is given on any current masthead page.

OM9704399