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A Dimeric Naphthyl Hydride Derivative of Zirconocene. Synthesis, Structure, and Chemical Properties

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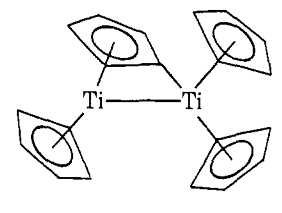
Abstract: Reduction of bis(η-cyclopentadienyl)zirconium dichloride with potassium naphthalene, at low temperatures in tetrahydrofuran, yields μ-(2-η^1:1-2-η^2-naphthyl)-hydrido-bis[bis(η-cyclopentadienyl)zirconium](*Zr–Zr*), $(\eta\text{-}C_5H_5)_2\overline{Zr(C_{10}H_7)(H)Zr}(\eta\text{-}C_5H_5)_2$ (hereinafter labeled I). The compound was characterized by a combination of chemical methods and X-ray crystallography. Crystals of I are orthorhombic, of space group *Pbca* (centrosymmetric), cell parameters a = 1.9243 (8), b = 2.0507 (6), and c = 1.1931 (8) nm, and contain eight molecules of $(C_5H_5)_4Zr_2(C_{10}H_7)(H)$ per unit cell. Key structural parameters follow: D(Zr–Zr) = 0.3307 (2), mean D(Zr–C_5H_5, centroid) = 0.255 (3), D(Zr–η^1-naphthyl, carbon) = 0.229 (1) nm. The hydrido ligand in I was not located by the X-ray work, but its presence was inferred from ^{1}NMR spectra in THF-d_8, which show a singlet at $\delta_{(CH_3)_4Si}$ −9.3. Reaction of I with excess CH_3I yields 1 mol CH_4/Zr_2 unit, which is in accordance with the monohydride structure. With HCl in THF, dicyclopentadienylzirconium dichloride, hydrogen, naphthalene, and a mixture of partially hydrogenated and hydrochlorinated naphthalenes are formed. Reaction of the complex with H_2 in THF yields naphthalene and dicyclopentadienylzirconium dihydride. In toluene and THF solutions, I is a catalyst for the hydrogenation of cyclohexene to cyclohexane.

Introduction

Low-valent bis(η-cyclopentadienyl)titanium[1] and bis(η-pentamethylcyclopentadienyl)titanium[2] and zirconium compounds[3] display unusual reactivity toward N_2, H_2, and CO, as well as interesting stoichiometric[4] and catalytic[5] reactions with olefins. The remarkable chemical reactivity of group 4B metallocenes toward small unsaturated molecules may be ascribed in part to the carbene-like character[6] of 14-electron, metal d^2, $(\eta\text{-}C_5H_5)_2M$ or $(\eta\text{-}C_5R_5)_2M$ species, where M is Ti, Zr, and Hf. Bis(η-pentamethylcyclopentadienyl)titanium, $[\eta\text{-}C_5(CH_3)_5]_2Ti$,[2a] has been prepared as a yellow-orange, crystalline solid from its dinitrogen derivative $[\eta\text{-}C_5(CH_3)_5]_4Ti_2N_2$. Bis($\eta$-pentamethylcyclopentadienyl)zirconium, $[\eta\text{-}C_5(CH_3)_5]_2Zr$, has not been isolated as a discrete compound, but is believed to be an intermediate in the decomposition of $[\eta\text{-}C_5(CH_3)_5]_4Zr_2(N_2)_3$.[3a] A characteristic property of low-valent titanium and zirconium metallocenes is the facile interaction of the metal with ligand hydrogens resulting in the formation of complex metal hydrides. Thus in solution, $[\eta\text{-}C_5(CH_3)_5]_2Ti$ rearranges reversibly to the tautomeric hydride, $[\eta\text{-}C_5(CH_3)_5][C_5(CH_3)_4CH_2]TiH$, and the effect is even more pronounced in the corresponding zirconium system.[2a,3a] With bis(η-cyclopentadienyl)titanium and -zirconium species, the rearrangement to complex metal hydrides is apparently irreversible. Titanocene, $(\eta\text{-}C_5H_5)_2Ti$, and zirconocene, $(\eta\text{-}C_5H_5)_2Zr$, are not known.[1,8] Reduction of $(\eta\text{-}C_5H_5)_2TiCl_2$ at ambient temperatures yields the fulvalene-bridged cyclopentadienyltitanium hydride complex: $\mu\text{-}(\eta^5\text{:}\eta^5\text{-}C_{10}H_8)\text{-}\mu(H)_2\text{-}[(\eta\text{-}C_5H_5)_2Ti]_2$ (II).[7] In an attempt to minimize the rearrangement of possible intermediate $(\eta\text{-}C_5H_5)_2Ti$ species, we reduced $(\eta\text{-}C_5H_5)_2TiCl_2$ at low temperatures and isolated the $\mu\text{-}(\eta^1\text{:}\eta^5\text{-}C_5H_4)(\eta\text{-}C_5H_5)_3Ti_2$ complex (III), which proved to be highly reactive toward N_2, H_2, and olefins.[1a,5a] We subsequently attempted the preparation of a similar zirconium complex (which we hoped might be even more reactive toward N_2, H_2, etc.) by reduction of $(\eta\text{-}C_5H_5)_2ZrCl_2$ with potassium naphthalene at low temperatures in tetrahydrofuran. A naphthyl hydride derivative of bis[bis(η-cyclopentadienyl)zirconium](*Zr–Zr*) was obtained. This paper describes the synthesis, molecular structure, and basic chemical properties of μ-(2-η^1:1-2-η^2-naphthyl)-hydrido-bis[bis(η-cyclopentadienyl)zirconium](*Zr–Zr*), $(\eta\text{-}C_5H_5)_2\overline{Zr(C_{10}H_7)(H)Zr}(\eta\text{-}C_5H_5)_2$ (I).



Results and Discussion

Preparation of $(\eta\text{-}C_5H_5)_2\overline{Zr(C_{10}H_7)(H)Zr}(\eta\text{-}C_5H_5)_2$ (I). Watt and Drummond[8] reported in 1966 that reduction of $(\eta\text{-}C_5H_5)_2ZrCl_2$ with sodium naphthalene yields a purple-black material assigned the formula $(C_5H_5)_2Zr$ on the basis of an infrared spectrum (which showed no apparent metal hydride absorptions) and elemental analyses. When Brintzinger and Bercaw[7a] later demonstrated that the "$(C_5H_5)_2Ti$" commonly

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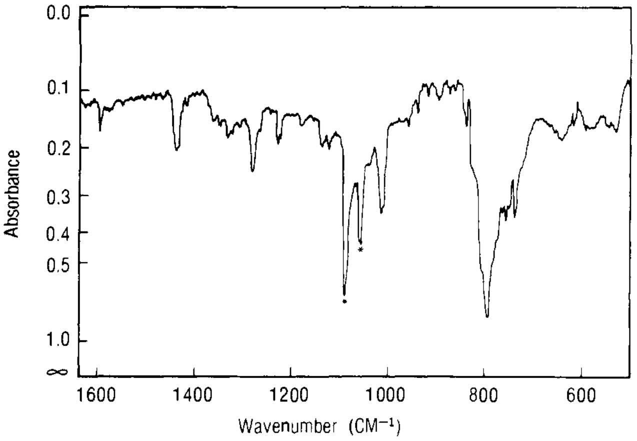

Figure 1. IR spectrum of I suspended in *n*-hexadecane-d_{34}. (Asterisks indicate absorptions of the *n*-hexadecane-d_{34}.)

Table I. Interatomic Bond Distances for $(\eta\text{-}C_5H_5)_2\overline{Zr(C_{10}H_7)(H)Zr}(\eta\text{-}C_5H_5)_2$ (I)

atoms	distances, nm
Zr(1)-Zr(2)	0.3307(2)
Zr(1)-Zr(2)	
Zr(1)-[C(1,1)-C(1,5)]	0.254 ± 0.003
Zr(1)-[C(3,1)-C(3,5)]	0.260 ± 0.003
Zr(1)-C(8)	0.2459(8)
Zr(1)-C(7)	0.2662(8)
Zr(2)-[C(2,1)-C(2,5)]	0.254 ± 0.003
Zr(2)-[C(4,1)-C(4,5)]	0.252 ± 0.003
Zr(2)-C(7)	0.229(1)
Zr(2)-C(6)	0.3334(9)
Zr(2)-C(8)	0.3289(8)
cyclopentadienyl C-C	0.141 ± 0.005
naphthalene C-C	0.141 ± 0.005

referred to in the literature is in fact the hydride $(C_5H_5)_2(C_{10}H_8)Ti_2H_2$ (II), it was suspected that the above zirconium compound might have an analogous composition. We repeated the synthesis of "$(C_5H_5)_2Zr$", as described in ref 8, using rigorously anaerobic conditions. A purple solid with (relatively broad) metallocene infrared absorptions at 800 and 1100 cm^{-1}, as well as a broad, intense metal hydride band at 1200-1500 cm^{-1}, was obtained. Brief exposure of the Nujol oil mull to air resulted in a total loss of the 1200-1500-cm^{-1} absorption. It appeared likely that the purple "$(C_5H_5)_2Zr$" compound was a zirconium hydride with complex cyclopentadienyl (e.g., C_5H_4) or fulvalenyl ($C_{10}H_8$) ligands. We were unable to further characterize this substance, and instead sought to prepare a simpler, coordinatively unsaturated $[(\eta\text{-}C_5H_5)_2Zr]_n$ species by the same low-temperature reduction technique used for the synthesis of $(C_5H_5)_3(C_5H_4)Ti_2$ (III).[1a]

Reaction of $(\eta\text{-}C_5H_5)_2ZrCl_2$ (1 mol) with potassium naphthalene (2 mol) at −80 °C in tetrahydrofuran over several days gave deep green solutions. After slow warming to room temperature and suitable workup, a dark green compound was isolated. Infrared spectra of the latter displayed sharp metallocene bands and no obvious metal hydride absorptions, and also suggested the presence of naphthalene.[9] The compound was purified to an extent, by washing with small aliquots of THF, and was then crystallized by slowly evaporating the (green) THF solutions at −13 °C. Elemental analyses of the crystals implied the composition $(C_5H_5)_4Zr_2C_{10}H_8$ (I). The infrared spectrum of I, taken in a perdeuterated *n*-hexadecane-d_{34} oil mull, is shown in Figure 1.

Other metal arene radical anion solutions were also tried for the reduction of $(\eta\text{-}C_5H_5)_2ZrCl_2$. Potassium anthracene at −111 °C gave deep green solutions which slowly decomposed at −80 °C and above. A brown-purple product, having an intense metal hydride absorption at 1100-1600 cm^{-1}, was isolated. With potassium biphenyl as the reducing agent, deep green solutions stable up to −35 °C were obtained. Upon warming to room temperature, only purple-colored solids with ν(Zr-H) at 1100-1600 cm^{-1} were obtained. Of the polynuclear aromatics studied only naphthalene seems capable of stabilizing the zirconocene moiety at ambient temperatures.

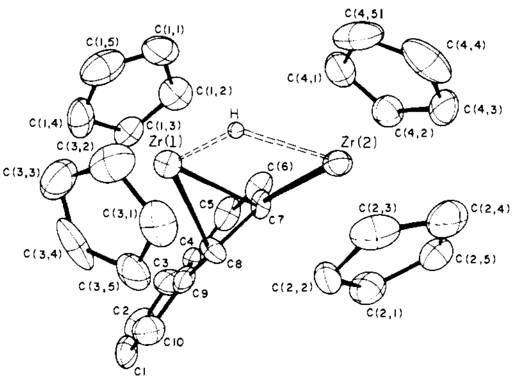

Figure 2. ORTEP plot of the structure of $(\eta\text{-}C_5H_5)_2\text{-}\overline{Zr(2\text{-}\eta^1\text{:}1\text{-}2\text{-}\eta^2\text{-}C_{10}H_7)(H)Zr}(\eta\text{-}C_5H_5)_2$ (I) (position of H ligand tentative). $D[Zr(1)\text{-}H]$ = 0.173 (7), $D[Zr(2)\text{-}H]$ = 0.226 (8) nm.

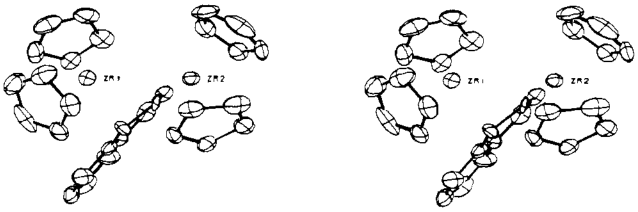

Figure 3. Stereoscopic view of I (Zr metal-naphthyl linkages and hydrido ligand are not shown).

Table II. Interatomic Bond Angles for I

angles	angle, deg
cyclopentadienyl C-C-C	108 ± 3
naphthalene C-C-C	120 ± 4
Cp(1)-Zr(1)-Cp(3)	123
Cp(2)-Zr(2)-Cp(4)	126
C(8)-C(7)-Zr(1)	65.4(1)
C(6)-C(7)-Zr(1)	120.9(5)
C(7)-C(8)-Zr(1)	82.1(1)
C(9)-C(8)-Zr(1)	128.5(4)
C(4)-C(7)-Zr(1)	102.1(1)
C(5)-C(8)-Zr(1)	111.7(5)
C(4)-C(7)-Zr(2)	172.5(1)
C(6)-C(7)-Zr(2)	125.6(1)
C(8)-C(7)-Zr(2)	121.1(1)

Crystal and Molecular Structure of $(\eta\text{-}C_5H_5)_2\overline{Zr(C_{10}H_7)(H)Zr}(\eta\text{-}C_5H_5)_2$ (I). Crystals of I were found to be orthorhombic, space group *Pbca* (centrosymmetric), *a* = 1.9243 (8), *b* = 2.0507 (6), *c* = 1.1931 (8) nm and eight molecules of $C_{20}H_{20}Zr_2C_{10}H_8$ per unit cell. The crystal structure was solved by standard heavy-atom methods and refined by full-matrix least-squares techniques to a standard *R* factor of 0.062. The molecular structure of I is shown in Figures 2 and 3. Molecular bond distances and angles are given in Tables I and II.

The molecule consists of a dimeric bis(η-dicyclopentadienylzirconium)(*Zr-Zr*) structure, with a naphthyl ($C_{10}H_7$) and a hydrido (H) ligand, bonded to the Zr-Zr framework

[($D_{\mathrm{Zr-Zr}}$ = 0.3307 (2) nm]. The four (η-cyclopentadienyl) ligands are bent back, symmetrically, from the direction of the metal–metal bond. The presence of (η-C_5H_5) cyclopentadienyl ligands is consistent with the infrared spectrum of the compound (Figure 1), which shows relatively sharp C–H (out-of-plane bending) and C–H (in-plane bending) modes at 795 and 1010 cm^{-1}, respectively. The observed mean, perpendicular zirconium-(η-C_5H_5) ring distance of 0.255 (3) nm is similar to the corresponding distance in (η-$C_5H_5)_3(\eta^1$-C_5H_5)Zr [0.258 (3) nm] and other zirconium metallocenes.[10] It is surprising to find normal (η-C_5H_5) bonding in (η-$C_5H_5)_4Zr_2(C_{10}H_7)$(H) (I) in view of the known very facile C–H insertion reaction of zirconium(II) with even pentamethylcyclopentadienyl ligands, as cited earlier. In the preparation of I, the tendency of $[(\eta\text{-}C_5H_5)_2Zr]_{n=1,2}$ intermediates to rearrange to complex metallocene hydrides is apparently satisfied by reaction with naphthalene giving a naphthyl hydride complex.

The naphthyl ligand in I is coordinated to both zirconium atoms: by an η^1-linkage from C(7) (the β-carbon atom of the naphthyl ring) to Zr(2), and by an apparent η^2-interaction of C(7) and C(8) (the β- and α-carbon atoms, respectively, of the same ring) with Zr(1). The Zr(2)–C(7), η^1 linkage is collinear with the C–H vector of the parent naphthalene. We could find no crystallographic evidence for the presence of a hydrogen atom in the vicinity of C(7). Atom C(7) is clearly σ bonded to Zr(2). The Zr(2)–C(7) distance of 0.229 (1) nm is similar to the zirconium-alkyl carbon bond lengths in $(\eta^5\text{-}C_9H_7)_2$-$Zr(CH_3)_2$ [0.2255 (5) nm] and (η-$C_5H_5)_2Zr[CH_2Si(CH_3)_2]_2$ [0.2280 (4) nm].[10] The Zr(1)–C(7,8) essentially η^2 linkage is associated with metal–carbon distances of Zr(1)–C(7), 0.2662 (8) nm, and Zr(1)–C(8), 0.2459 (8) nm. As a consequence of the η^1:η^2 coordination, the zirconium-bonded carbon atoms C(7) and C(8) are slightly distorted out of the plane of the nonbonded naphthyl ligand atoms C(1–6), C(9), and C(10). Atom C(7) is distorted at a perpendicular distance of 0.1049 (9) nm from the plane, away from Zr(1), whereas C(8) is a distance of 0.0052 (9) nm from the plane, approximately in the direction of Zr(1). The distortion of an aromatic ligand is a characteristic of localized coordination and is seen, for example, in (1-4-η^4-naphthalene)(dmpe)$_2$TaCl [dmpe ≡ 1,2-bis(dimethylphosphino)ethane], where the η^4-coordinated diene unit of naphthalene is at an angle of 43.3° from the plane of the nonbonded naphthalene carbon atoms.[11] In the zirconium complex I, the distortion of the naphthyl ligand is much less, presumably because of the simultaneous η^1 and η^2 coordination.

The expected hydrido ligand in I could not be definitely located by crystallographic methods (see Experimental Section). Evidence for a metal hydride in I has been obtained from ^{1}H NMR spectra, which show a singlet at $\delta_{(CH_3)_4Si}$ −9.3, and from the chemical reactivity of the molecule with HCl and CH_3I (see below). However, metal hydride absorptions are not evident in the infrared spectrum of I (Figure 1). Vibrational modes of bridging monohydride species are often very weak and broad in the infrared.[12]

The structure of I is unusual in having normal cyclopentadienyl rings and in possessing a multiply coordinated naphthyl ligand. Several examples of complexes with σ-bonded[13] and localized π-bonded[14] aromatic ligands are known. In the structure of I we find a hitherto unobserved, simultaneous σ and π, metal coordination of an aromatic molecule. The naphthyl hydride configuration presumably arises from a formal insertion of a divalent zirconium intermediate [i.e., (η-$C_5H_5)_2$Zr], formed in the reduction of (η-$C_5H_5)_2ZrCl_2$, into the C–H bond of naphthalene. The structure of I is reminiscent of *cis*-bis[1,2-bis(dimethylphosphino)ethane](2-η^1-naphthyl)hydridoruthenium(II), which provided one of the earliest examples of a formal insertion of a low-valent metal [i.e., Ru(0)] into the C–H bond of an aromatic molecule.[15]

Chemical Properties of (η-$C_5H_5)_2Zr(C_{10}H_7)(H)Zr(\eta$-$C_5H_5)_2$ (I). The title complex is slightly soluble in THF and to a lesser extent in toluene. Although the solid may be kept indefinitely under an inert atmosphere at ambient temperatures, its solutions are unstable and on standing for 10–24 h decompose, giving blue- or purple-colored, complex cyclopentadienylzirconium hydrides (having intense, broad infrared absorptions at 1200–1500 cm^{-1}). ^{1}H NMR spectra of I in THF-d_8 have been recorded and are assigned as follows: $\delta_{(CH_3)_4Si}$ 6.0 (η-C_5H_5), 5–8 (η^1:η^2-naphthyl), and −9.3 (Zr–H). Decomposition products in THF-d_8 gave only a broad, featureless NMR signal at $\delta_{(CH_3)_4Si}$ 4–9.

Reaction of I with excess methyl iodide yields 1 mol of CH_4 per mol of complex, which is consistent with the presence of one hydrido ligand per Zr_2 unit. Solutions of I in THF react with HCl gas at −80 to 0 °C, giving somewhat less than the expected 1 mol of H_2 per mol of complex. Other products are (η-$C_5H_5)_2ZrCl_2$, a mixture of dihydronaphthalene, tetrahydronaphthalene, and naphthalene, and smaller quantities of hydrochlorinated naphthalenes:

$$(C_5H_5)_4Zr_2(C_{10}H_7)(H) \xrightarrow[\text{THF}]{\text{HCl}} H_2 + (C_5H_5)_2ZrCl_2$$
$$+ [C_{10}H_{10} > C_{10}H_{12} > C_{10}H_8] + C_{10}H_9Cl, \text{etc.}$$

The hydronaphthalenes are presumably formed by the successive protonation of the relatively electron-rich (η^1:η^2-naphthyl) ligand. Some naphthalene and hydronaphthalenes may also be formed by direct hydride transfer from zirconium to the naphthyl ligand; this could account for the less than stoichiometric amount of H_2 evolved. The formation of hydronaphthalenes is interesting in that the process is analogous to a Birch reduction,[16] except that in this case the reducing agent is divalent zirconium.

Solutions of crystalline I in toluene do not react with N_2 (10 atm, 23 °C) in contrast to the remarkable sensitivity of μ-(η^1:η^5-C_5H_4)(η-$C_5H_5)_3Ti_2$ (II) for N_2. This is not surprising since I does not contain an (η-$C_5H_5)_2Zr^{II}$ unit. The [η-$C_5(CH_3)_5]_2Zr^{II}$ species is highly reactive toward N_2.[3a–c] Note, however, that [(η-$C_5H_5)_2Zr^{III}R$] [R = $(Me_3Si)_2CH$] forms an N_2 derivative.[17] Treatment of a deep green THF solution of I with H_2 (2.7 atm) at first yields a clear, colorless solution and, upon further reaction, naphthalene and a white precipitate which consists mainly of polymeric (η-$C_5H_5)_2ZrH_2$ are obtained. In a related reaction, [η-$C_5(CH_3)_5]_4Zr_2(N_2)_3$ with H_2 yields [η-$C_5(CH_3)_4]_2ZrH_2$ and N_2.[3d] In contrast, μ-(η^1:η^5-C_5H_4)(η-$C_5H_5)_3Ti_2$ (II) reversibly reacts with H_2 giving the green-gray $(C_{10}H_{10}TiH)_n$ or $(C_{10}H_9TiH_2)_n$ hydride adduct.[5a] Solutions of I in THF or toluene catalyze the hydrogenation of cyclohexene to cyclohexane (23 °C, 1 atm H_2). The toluene solutions are somewhat more active: ~50 mol of olefin is hydrogenated per mol of catalyst over 48 h. As a cyclohexene hydrogenation catalyst, I is much less effective than μ-(η^1:η^5-C_5H_4)(η-$C_5H_5)_3Ti_2$ (II).[5a]

Conclusions

The results of this investigation emphasize a number of differences in the organometallic chemistry of zirconium vis-à-vis that of titanium. There is a normal (η-C_5H_5)-metal bonding in I while in (η-$C_5H_5)_2Ti^{II}$ compounds the facile C–H insertion reaction of the cyclopentadienyl group possibly precludes interaction with naphthalene. The formation of a strong σ–π bond to the naphthalene group via oxidative addition to an aromatic C–H bond by the (Zr–Zr) moiety is undoubtedly a factor in this respect. This unusual configuration also readily leads to the observed reduction of naphthalene to hydronaphthalenes by HCl.

A second obvious difference in the zirconium chemistry compared to the analogous chemistry of titanium which is brought out by this study is the greater stability of the Zr–H bond. Low-valent zirconium metallocenes decompose more readily to yield complex metal hydrides. Zr(II) and Zr(III) species are irreversibly oxidized to Zr(IV) by hydrogen, and consequently are poorer hydrogenation catalysts.

Experimental Section

Most of the organometallics used in this work are highly air sensitive and were handled by a combination of argon drybox and high vacuum line techniques. Details of our general experimental procedures, including methods for the preparation of solvents and recording IR spectra, are given in ref 1a and 5a. ^{1}H NMR spectra were recorded on a Jeolco FX-100 spectrometer.

Preparation of $(\eta\text{-}C_5H_5)_2\overline{Zr(C_{10}H_7)(H)Zr}(\eta\text{-}C_5H_5)_2$ (I). The synthesis depends on the reaction of $(C_5H_5)_2ZrCl_2$ with potassium naphthalene in tetrahydrofuran at low temperatures. A special apparatus designed for stirring solutions for extended periods of time, at low temperatures, was employed (see Experimental Section in ref 1a). The lower 1-L bulb of the apparatus was charged (in an Ar atmosphere) with solid droplets of potassium (8.0 g, 0.205 mol) and naphthalene (46 g, 0.36 mol). Finely ground $(C_5H_5)_2ZrCl_2$ (ROC/RIC) (29.9 g, 0.102 mol) was loaded in the addition funnel. Tetrahydrofuran (300 mL) was added and the $K/C_{10}H_8$ mixture stirred until formation of green potassium naphthalene was complete. The reactor was then immersed in liquid N_2 and the $(C_5H_5)ZrCl_2$ slowly released onto the frozen radical-anion solution. Additional THF (400–500 mL) was distilled over the mixture at −196 °C. The apparatus was warmed to the melting point of THF and the resulting slush (at ca. −110 °C) vigorously agitated and allowed to warm to −80 °C. It was left stirring for 14 days at −80 °C, during which the color of the mixture turned from deep brown to green. It was then warmed slowly to room temperature: at −45 °C (1 day), −23 °C (18 h), then quickly to ~23 °C. (In some cases, the green color appeared only upon warming from −80 to −45 °C.) The deep green solution at room temperature was filtered cold (−20 to −80 °C) to minimize decomposition. The filtrate was evaporated to dryness and pumped at $<10^{-4}$ Torr for 6–8 h at 25 °C to remove excess naphthalene. The dark residue was washed, quickly, with 100 mL of toluene. A dark green, almost black, solid (18 g) was obtained.

This crude product was purified by solvent extraction and crystallization as follows. An apparatus consisting of three vertical tubes (A, B, and C, each of 80-cm^3 capacity), connected by horizontal arms containing a filter disk, was used. It was charged (in the middle leg, B) with crude complex (3 g) and THF (45 mL). The mixture was stirred, and allowed to settle, and the largely purple-colored supernatant liquid was decanted into leg C. The remaining solid was washed with THF (10 mL) until the solutions were a deep green. Most of this solid was dissolved in THF (110 mL) and filtered into leg A. This filtrate was cooled to −13 °C and slowly evaporated to near dryness at ~−13 °C over 20–30 days. The very dark crystals formed were washed with isopentane. Yield was 0.58 g (crystals stored under Ar at 5 °C). Anal. Calcd for $C_{30}H_{28}Zr_2$: C, 63.11; H, 4.94; Zr, 31.95. Found: C, 64.13; H, 4.99; Zr, 30.79.

Collection of X-ray Data and Structure Determination. A crystal approximately 0.275 × 0.275 mm in cross section and 0.125 mm in length was sealed under an inert atmosphere in a 0.5-mm quartz capillary. The crystal was held in place in the capillary by a very small amount of Apiezon L grease. Preliminiary precession photographs showed the crystal structure to be orthorhombic and the observed systematic absences $hk0$, $h + l = 2n + 1$, $0kl$, $k + l = 2n + 1$, and $h0l$, $h + l = 2n + 1$, uniquely determine the space group as *Pbca*.

The crystal was mounted on a computer controller Picker FACS-I four-circle X-ray diffractometer for further analysis. The system used Mo Kα radiation (0.071 069 nm) from a pyrolytic graphite monochromator (002), a 1.7° takeoff angle, and a scintillation counter. Thirty reflections which were above 30° in 2θ were carefully centered and their settings refined by a least-squares technique to determine accurate cell dimensions at 23 °C. These are a = 1.9243 (8) nm, b = 2.0507 (6) nm, c = 1.1931 (8) nm, and V = 4.708 17 nm^3.[18] The crystal was found to be of good quality with an ω-scan width at half-height of 0.15–0.20° for several intense reflections.

Data were collected using a θ–2θ scan technique with a scan rate of 2°/min (in 2θ) to measure all reflections with $4° \leq 2\theta \leq 50°$. Individual reflections were scanned from 0.6° above to 0.6° below the Mo Kα maximum. Background counts were measured for 10 s at each end of the scanned range. Three standard reflections were measured every 100 reflections to assess crystal decomposition and movement. Two full forms of data were collected. During data collection in the first form, the standard reflections showed only a slight and random variation. During data collection in the second form, a decrease in standard intensities was noted. Investigation showed the decrease to result from slight movement of the crystal. The crystal was carefully realigned and all reflections affected by the misalignment were remeasured. Data from the first form consisted of 4233 reflections of which 1292 were judged to be observed by the criteria $(|F_o|)^2 \geq 3\sigma(|F_o|)^2$. This full data set was used in Patterson and Fourier syntheses and the observed reflections were used in the initial stages of least-squares refinement. Final refinement was based on a "best" data set obtained by averaging the equivalent reflections from both collected forms. This procedure reduced the total of 4233 measured reflections to a set of 4057 unique reflections of which 3018 were judged observed as before. Data were corrected for Lorentz, polarization, and absorption effects, the latter based on a calculated linear absorption coefficient of 8.850 cm^{-1}.

Solution and Refinement of the Structure. The structure was refined using full-matrix least-squares techniques minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, and the weight, w, is $4(F_o)^2/\sigma^2(F_c)^2$. The agreement indices R and R_w are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$. The atomic scattering factors for all atoms were obtained from the compilations of Cromer and Waber,[19] and the anomalous dispersion terms for Zr were taken from the compilation of Cromer and Liberman.[20]

The zirconium atoms were easily located from a three-dimensional Patterson map. With these atoms as input and using a unit weighting scheme, one cycle of least-squares refinement gave the agreement index 0.543. The locations of the cyclopentadienyl carbon atoms and the carbon atoms of the one naphthalene molecule were determined from the subsequent synthesis of a three-dimensional Fourier map. Several cycles of least-squares refinement with these atoms input and using a statistical weighting scheme gave the value R = 0.162. At this point a difference Fourier map was synthesized. The most intense peak which appeared was 1043 e/nm^3 and this and several other peaks in the range 984–853 e/nm^3 were closely associated with the zirconium atoms. ORTEP drawings[21] of the partially refined structure showed the molecule to be dimeric with the naphthalene molecule apparently σ bonded to one of the zirconium atoms. The difference Fourier did not clearly establish the location of the cyclopentadienyl or naphthalene hydrogen atoms. Therefore, the hydrogen atoms were included at idealized positions with C–H bond distance of 0.095 nm. With all atoms input, the inclusion of anisotropic temperature factors, and using the full averaged data set, eight cycles of least-squares refinement led to convergence giving the final agreement indices R = 0.062 and R_w = 0.042 for the observed reflections and R_w = 0.061 for all reflections.

A final difference Fourier was calculated using only the data for $(\sin\theta)/\lambda < 0.35$ in order to determine if there is a hydrogen atom associated with either of the two zirconium atoms. The most intense peak which appeared was 1575 e/nm^3. Approximately ten peaks in the range 1097–997 e/nm^3 were correlated with the two zirconium atoms. Only one of these peaks was consistent with known metal hydride distances. An attempt was made to refine the structure placing a bridging hydride in this position. The hydride position as shown in the ORTEP plot in Figure 2 was chosen on the basis of this final difference Fourier but was not confirmed by least-squares analysis. Further attempts in confirming the position of the hydride were unsuccessful.

Reactivity of $(\eta\text{-}C_4H_5)_4Zr_2(C_{10}H_7)(H)$ (I) with Methyl Iodide. A 30-cm^3 reactor tube, equipped with a Teflon stopcock and glass stir bar, was charged with crystals of I (46.17 mg, 0.0809 mmol). Methyl iodide (2 mL) was distilled over the crystals at −196 °C. The mixture was warmed and allowed to react at −18 °C for 1.5 h (pale yellow solution) and then at 23 °C for 18 h. Methane (0.0794 mmol) was collected with a Toepler pump, molar ratio CH_4:I = 0.98.

Reactivity of I with HCl in THF. Crystalline I (55.44 mg, 0.0971 mmol) contained in a reactor tube was dissolved in THF (4 mL), the solution was cooled to −196 °C, and ~1 mmol of dry, O_2-free HCl was added. The mixture was stirred for 30 min at −80 °C (yellow-orange), then 30 min at 0 °C (clear, colorless). Hydrogen (0.0782 mmol) was collected, ratio H_2:I = 0.81. Organic products were isolated by distillation under vacuum, and were identified by standard GC/mass spectrum techniques. The reaction was found to yield a mixture of dihydronaphthalene, $C_{10}H_{10}$ (48% w/w), tetrahydronaphthalene, $C_{10}H_{12}$ (37%), naphthalene, $C_{10}H_8$ (8%), and a mixture of hydrochlorinated naphthalenes (total of ~7%). The white solid residue in the reactor tube was identified as $(\eta\text{-}C_5H_5)_2ZrCl_2$ by its infrared and mass spectrum. In another, similar experiment 53.21 mg (0.0932 mmol) of I was reacted with HCl, giving 0.0677 mmol of H_2, ratio H_2:I = 0.71. A mixture of naphthalenes (10 mg) was found, $C_{10}H_{10}$ (55%), $C_{10}H_{12}$ (32%), and $C_{10}H_8$ (13%); the hydrochloronaphthalenes were not determined in this analysis.

Reaction of I with Hydrogen. A solution of I (53.81 mg, 0.0942 mmol) in THF (4 mL) was stirred under hydrogen (2.7 atm, 23 °C). The deep green color was slowly discharged and after ~4 h a clear, almost colorless solution was obtained. Upon prolonged stirring under H_2 (18 h), a white precipitate (IV) appeared. The mixture was warmed up to 40 °C and all volatiles removed under vacuum and analyzed by GC (10% Carbowax 20M on Chromosorb W AW, 90-220 °C). Naphthalene (5 mg, 0.040 mmol) was detected; there was no trace of hydrogenated naphthalenes. The white solid IV was treated with HCl (1 mmol) in THF (4 mL) at −80 °C (0.5 h) and then at 0 °C (0.5 h). Hydrogen (0.245 mmol) was evolved, ratio H_2:Zr_2 = 2.6. The yellowish-white organometallic residue was identified by its infrared spectrum as $(\eta\text{-}C_5H_5)_2ZrCl_2$.

In another experiment, the white solid (IV) obtained as above was treated with an excess of methyl iodide (18 h, 23 °C). Methane evolved: 3.0 mol/Zr_2 unit in I. An infrared spectrum of IV suspended in *n*-hexadecane-d_{34} oil showed $(\eta\text{-}C_5H_5)$ ligand absorptions at (cm^{-1}) 3050 (w), 1012 (m), 828 (m), 800 (s), 780 (m), Zr-H absorptions (cm^{-1}) at 1525 (m, broad, width at ½ height ~50 cm^{-1}), 1325 (s, broad, width at ½ height ~100 cm^{-1}). When IV was prepared by treatment of I with D_2, the metal hydride frequencies were shifted to 1100 and 960 cm^{-1}, respectively. The infrared spectrum of IV is identical with that of a bona fide sample of $[(\eta\text{-}C_5H_5)_2ZrH_2]_n$[21] [prepared from $(\eta\text{-}C_5H_5)_2Zr(BH_4)_2$];[22] however, the IR of IV also displays two sharp, weak to medium intensity bands at 480 and 789 cm^{-1}. These frequencies are characteristic of the most intense naphthyl or naphthalene absorptions (see Figure 1). The solid IV may thus contain some dicyclopentadienylzirconium naphthyl species, but, from its infrared spectrum and the stoichiometry of its reactions with HCl and CH_3I, it appears to be mainly $[(\eta\text{-}C_5H_5)_2ZrH_2]_n$.

Catalytic Hydrogenation of Cyclohexene. A solution of crystalline I (20 mL) in toluene (5 mL) and cyclohexene (1 mL) was stirred for 48 h under an initial H_2 pressure of 786 Torr. A pressure drop was noted and the color of the solution changed from a deep to a light yellow-green during this time. Products were analyzed by GC/mass spectroscopy. Found: cyclohexane 54 mol/mol I, naphthalene ~0.6 mol/mol I, no trace of hydrogenated naphthalenes.

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Supplementary Material Available: Lists of refined positional and thermal parameters for all the atoms and tables of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

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