Synthesis and Structures of Neutral and Cationic *rac*-(Ethylenebis(tetrahydroindenyl))zirconium(IV) Benzyl Complexes

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Reaction of *rac*-(ethylenebis(tetrahydroindenyl))$ZrCl_2$ (1) with 2 equiv of K[CH_2Ph] produces the dibenzyl complex (ethylenebis(tetrahydroindenyl))$Zr(CH_2Ph)_2$ (2). Reaction of 2 with [$(C_5H_4Me)_2Fe$][BPh_4] yields the cationic complex [(ethylenebis(tetrahydroindenyl))$Zr(CH_2Ph)(THF)$][BPh_4] (3). In CH_3CN solvent, 3 undergoes ligand substitution to yield [(ethylenebis(tetrahydroindenyl))$Zr(\eta^2\text{-}CH_2Ph)(CH_3CN)$][$BPh_4$] (4). The structures of 2 and 4 have been determined by X-ray diffraction. Complex 2 crystallizes in space group *Pbcn* with a = 10.008 (3) Å, b = 14.895 (4) Å, c = 17.532 (6) Å, V = 2613.5 (2.4) Å^3, and Z = 4. The benzyl ligands are undistorted and are rotated to conformations that minimize steric interactions with the $(CH_2)_4$ rings of the (ethylenebis(tetrahydroindenyl))Zr framework. Complex 4 crystallizes in space group $P\bar{1}$ with a = 12.300 (2) Å, b = 12.493 (2) Å, c = 16.633 (3) Å, α = 84.61 (1)°, β = 71.18 (1)°, γ = 69.42 (1)°, V = 2264.1 (9) Å^3, and Z = 2. The CH_2Ph ligand of 4 is bonded in a η^2 mode with a weak Zr–Ph interaction. The (ethylenebis(tetrahydroindenyl))Zr framework of 4 is distorted relative to that of 2 to minimize steric interactions between a $(CH_2)_4$ ring and the η^2-CH_2Ph ligand.

Cationic, 14-electron, metal–alkyl complexes $Cp_2M(R)^+$ (M = Ti, Zr, Hf) have been implicated as active species in metallocene-based Ziegler–Natta olefin polymerization and hydrooligomerization catalyst systems, including the classical Cp_2MX_2/AlR_nX_{3-n} systems, the recently developed Cp_2MX_2/alumoxane systems, and supported actinide $(C_5Me_5)_2MR_2$ catalyst systems.[1-3] Related 16-electron complexes $Cp_2Zr(R)(L)^+$ containing a labile ligand L (e.g. THF, α-picoline, etc.) catalyze the dimerization and polymerization of ethylene as well as the coupling of olefins with substituted pyridines[1c,4,5] and undergo a variety of stoichiometric insertion, β-H elimination, and σ-bond metathesis reactions.[6,7] Chiral $Cp_2M(R)(L)^+$ complexes are of interest for asymmetric catalysis and as model systems for the study of stereoselectivity in insertion and polymerization reactions.

Early work on chiral Cp_2MX_2 systems focused on compounds containing a chiral substituent on one or both of the Cp ligands and on compounds containing a chiral metal center (i.e. four different substituents).[8] More recently, Brintzinger has developed a new class of ansa-metallocene complexes that contain strategically substituted Cp ligands linked by an CH_2CH_2 or $CH_2CH_2CH_2$ bridge.[9,10] The ethylene-bridged systems (EBTHI)MCl_2 (M = Ti, Zr, Hf; EBTHI = ethylenebis(tetrahydroindenyl) adopt chiral C_2 structures in which the chirality is associated with the metal–ethylenebis(tetrahydroindenyl) linkage and is unaffected by exchange of the X ligands. These complexes, in conjunction with alumoxane cocatalysts, exhibit high stereoselectivity in catalytic α-olefin polymerizations and hydrooligomerizations, in which chiral (EBTHI)$M(R)^+$ ions are presumed to be the active species.[2d,e,9d,11,12] The Ti

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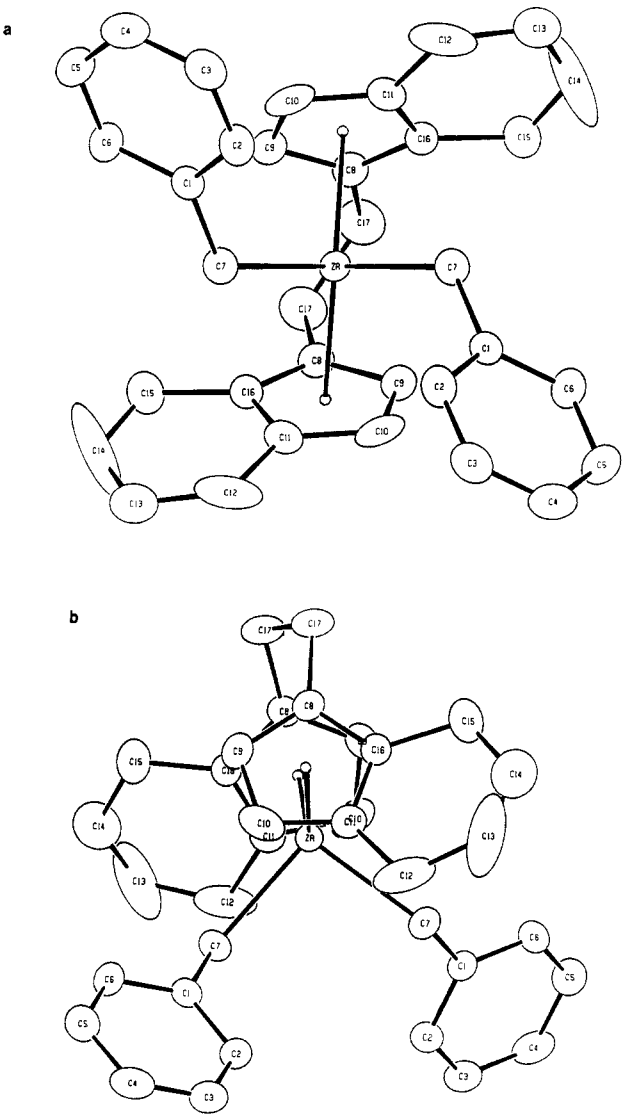


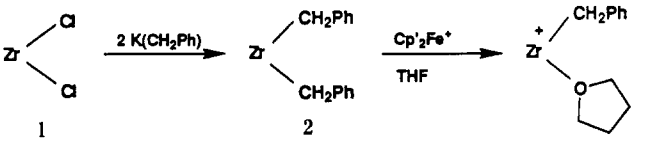
Figure 1. Molecular structure and numbering scheme of (EBTHI)Zr(CH_2Ph)$_2$ (**2**): (a) view down the C_2 axis; (b) view perpendicular to the Bz–Zr–Bz plane.

system has also been used in the diastereoselective synthesis of homoallylic alcohols.[13] Paquette and Vollhardt have prepared C_2 symmetric titanocene and zirconocene complexes that incorporate chiral, rigid Cp ligands and that catalyze the enantioselective hydrogenation of simple prochiral alkenes.[14,15]

We have chosen to use Brintzinger's (EBTHI)Zr system in our initial efforts to synthesize chiral $Cp_2Zr(R)(L)^+$ complexes because of the synthetic accessibility and previous applications in catalysis of the parent dichloride complex (EBTHI)$ZrCl_2$ (**1**).[9] In this paper we describe the synthesis and structures of neutral and cationic *rac*-(EBTHI)Zr^{IV} benzyl complexes.

Results and Discussion

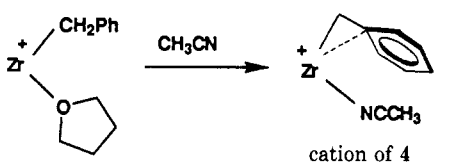
Synthesis of Neutral and Cationic (Ethylenebis(tetrahydroindenyl))zirconium(IV) Benzyl Complexes. Reaction of *rac*-(EBTHI)$ZrCl_2$ (**1**) with 2 equiv of K[CH_2Ph] in THF at 0 °C produces the dibenzyl complex *rac*-(EBTHI)Zr(CH_2Ph)$_2$ (**2**) as a sparingly soluble yellow solid (74%, eq 1, in which Zr = (EBTHI)Zr).



1 2 cation of **3**

(1)

Complex **2** was isolated from the KCl coproduct by Soxhlet extraction with toluene and characterized by NMR spectroscopy, X-ray diffraction, and analysis. The use of K[CH_2Ph] rather than Mg(CH_2Ph)Cl facilitates product isolation and has been previously applied to the synthesis of related Zr and Hf benzyl complexes.[16] In the present case, the product is easily isolated free of halide as required for the success of the subsequent oxidative-cleavage reaction. Reaction of **2** with [(C_5H_4Me)$_2$Fe][BPh_4] in THF (24 °C, 30 min) yields [(EBTHI)Zr(CH_2Ph)(THF)][BPh_4] (**3**), which is isolated (76%) as an analytically pure orange solid by precipitation from THF/toluene (eq 1). This reaction involves net oxidative cleavage of a Zr–CH_2Ph bond and yields bibenzyl as the sole organic product, presumably via coupling of benzyl radicals. The choice of BPh_4^- as a noncoordinating, nonreactive counterion was based on earlier observations that anions such as PF_6^-, BF_4^-, $CF_3SO_3^-$, etc. invariably react with or coordinate strongly to $Cp_2Zr(R)^+$ ions.[6a,17] Isolated **3** is only sparingly soluble in THF or CH_2Cl_2 but forms a more soluble CH_3CN complex, [(EBTHI)Zr(η^2-CH_2Ph)(CH_3CN)][BPh_4] (**4**), in CH_3CN solvent (eq 2).



cation of **3** cation of **4**

(2)

Solid-State Structures of 2 and 4. The solid-state structures of **2** and **4** were determined by X-ray diffraction and are illustrated in Figures 1 and 2. Bond distances and angles are given in Tables I and II, and atomic coordinates are listed in Tables III and IV.

Views down the crystallographically imposed C_2 axis and perpendicular to the Bz–Zr–Bz plane of **2** are shown in Figure 1. The (EBTHI)Zr framework is essentially isostructural with that of the dichloride analogue **1**.[9] The Zr–Cp centroid distances (2.226 Å) and the Cp–Zr–Cp angle (124.4°) are nearly identical with those of **1** (2.22 Å, 125.0°), and for both compounds the Zr–C distances to the carbons substituted by the $(CH_2)_4$ ring are relatively long. The Bz–Zr–Bz angle of **2** (95.2°) is close to the Cl–Zr–Cl angle of **1** (98.6°). The ethylenebis(tetrahydroindenyl) ligand of **2** adopts a conformation in which the $(CH_2)_4$ rings project forward over the two "equatorial" coordination sites (between the Cp rings), again similar to that of **1**. The benzyl ligands have normal undistorted η^1 structures (Zr–Cl = 3.393 (4) Å, Zr–C7–C1 = 125.6 (2)°) and are bent away from the sterically bulky $(CH_2)_4$ rings of the ethylenebis-

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Table I. Selected Interatomic Distances and Bond Angles for (EBTHI)Zr(CH_2Ph)$_2$ (2)[a]

Bond Distances (Å)			
Zr–C7	2.314 (4)	C5–C4	1.379 (6)
Zr–C8	2.497 (4)	C8–C9	1.389 (6)
Zr–C9	2.448 (4)	C8–C16	1.391 (6)
Zr–C10	2.516 (4)	C8–C17	1.526 (7)
Zr–C11	2.596 (4)	C9–C10	1.399 (7)
Zr–C16	2.561 (4)	C10–C11	1.425 (7)
Zr–C1C	2.226	C11–C12	1.512 (7)
C1–C2	1.396 (6)	C11–C16	1.389 (6)
C1–C6	1.381 (6)	C12–C13	1.470 (12)
C1–C7	1.477 (6)	C13–C14	1.312 (14)
C2–C3	1.377 (7)	C14–C15	1.459 (12)
C6–C5	1.387 (7)	C15–C16	1.496 (6)
C3–C4	1.359 (7)	C17–C17′	1.505 (10)
Zr–C1	3.391 (4)		

Bond Angles (deg)			
C7–Zr–C7′	94.7 (2)	C1–C6–C5	121.0 (4)
C7–Zr–C1C	106.1	C2–C3–C4	121.3 (4)
C7–Zr–C1C′	110.6	C6–C5–C4	120.4 (5)
C7′–Zr–C1C	110.6	C3–C4–C5	118.9 (5)
C7′–Zr–C1C′	106.1	C16–C8–C17	125.1 (4)
C1C–Zr–C1C′	124.4	C16–C8–C9	108.1 (4)
Zr–C7–C1	125.6 (2)	C17–C8–C9	126.7 (4)
C7–C1–C2	121.6 (4)	C8–C9–C10	108.2 (4)
C7–C1–C6	121.0 (4)	C9–C10–C11	107.7 (4)
C6–C1–C2	117.3 (4)	C10–C11–C12	129.4 (5)
C1–C2–C3	120.9 (4)	C10–C11–C16	107.1 (4)
C12–C11–C16	122.7 (5)	C8–C16–C11	108.9 (4)
C11–C12–C13	110.9 (6)	C8–C16–C15	127.7 (4)
C12–C13–C14	123.0 (7)	C11–C16–C15	122.7 (4)
C13–C14–C15	126.7 (8)	C8–C17–C17′	110.1 (3)
C14–C15–C16	110.9 (6)		

[a] *C*n*C* denotes the centroid of the C_5 ring.

Table II. Selected Interatomic Distances and Bond Angles for [(EBTHI)Zr(CH_2Ph)(CH_3CN)][BPh_4] (4)[a]

Bond Distances (Å)			
Zr–C7	2.321 (9)	Zr–N	2.281 (9)
Zr–C11	2.505 (8)	Zr–C21	2.492 (9)
Zr–C12	2.429 (8)	Zr–C22	2.461 (9)
Zr–C13	2.501 (8)	Zr–C23	2.537 (9)
Zr–C14	2.588 (9)	Zr–C24	2.584 (9)
Zr–C15	2.558 (9)	Zr–C25	2.522 (9)
Zr–C1C	2.218	Zr–C2C	2.218
C1–C2	1.417 (13)	C3–C4	1.381 (14)
C1–C6	1.402 (13)	C5–C4	1.372 (13)
C1–C7	1.476 (13)	N–C8	1.116 (11)
C2–C3	1.374 (14)	C8–C9	1.443 (15)
C6–C5	1.400 (14)	Zr–C1	2.627 (9)
C11–C12	1.398 (12)	C21–C22	1.413 (13)
C11–C15	1.399 (12)	C21–C25	1.413 (12)
C11–C10	1.505 (13)	C21–C20	1.517 (13)
C12–C13	1.402 (12)	C22–C23	1.386 (13)
C13–C14	1.383 (12)	C23–C24	1.398 (13)
C14–C19	1.495 (14)	C24–C29	1.504 (14)
C14–C15	1.417 (13)	C24–C25	1.422 (13)
C19–C18	1.532 (19)	C29–C28	1.522 (17)
C18–C17	1.455 (20)	C28–C27	1.457 (17)
C17–C16	1.488 (16)	C27–C26	1.529 (17)
C16–C15	1.526 (13)	C26–C25	1.498 (14)
C10–C20	1.536 (13)		

Bond Angles (deg)			
N–Zr–C7	114.9 (3)	C7–C1–C6	121.4 (9)
N–Zr–C1C	102.7	C6–C1–C2	117.8 (9)
N–Zr–C2C	102.8	C1–C2–C3	120.2 (9)
C7–Zr–C1C	106.8	C1–C6–C5	120.2 (9)
C7–Zr–C2C	105.3	C2–C3–C4	120.7 (9)
C1C–Zr–C2C	124.7	C6–C5–C4	121.0 (9)
Zr–C7–C1	84.4 (5)	C3–C4–C5	119.0 (9)
C7–C1–C2	120.6 (9)		
C10–C11–C15	126.7 (8)	C20–C21–C25	127.8 (8)
C15–C11–C12	106.3 (8)	C25–C21–C22	107.2 (8)
C10–C11–C12	127.0 (8)	C20–C21–C22	125.1 (9)
C11–C12–C13	109.4 (8)	C21–C22–C23	109.4 (9)
C12–C13–C14	107.9 (8)	C22–C23–C24	107.7 (9)
C13–C14–C19	130.8 (9)	C23–C24–C29	129.7 (10)
C13–C14–C15	107.5 (8)	C23–C24–C25	108.6 (8)
C19–C14–C15	120.4 (9)	C29–C24–C25	121.4 (9)
C14–C19–C18	112.1 (10)	C24–C29–C28	109.3 (9)
C19–C18–C17	116.5 (10)	C29–C28–C27	114.2 (10)
C18–C17–C16	112.8 (12)	C28–C27–C26	115.2 (10)
C17–C16–C15	111.3 (10)	C27–C26–C25	111.8 (9)
C11–C15–C14	108.9 (8)	C21–C25–C24	107.0 (8)
C11–C15–C16	126.6 (9)	C21–C25–C26	127.8 (9)
C14–C15–C16	123.7 (9)	C24–C25–C26	123.7 (9)
C11–C10–C20	111.0 (7)	C21–C20–C10	110.1 (8)

[a] *C*n*C* denotes the centroid of the C_5 ring.

(tetrahydroindenyl) ligand. Figure 1a illustrates in a dramatic way the directing ability of this ligand system.

The structure of cationic benzyl complex **4** (Figure 2) differs from that of **2** in both the nature of the benzyl ligation and the conformation of the ethylenebis(tetrahydroindenyl) ligand. Complex **4** contains a distorted η^2-benzyl ligand similar to that found earlier for the analogous Cp complex $Cp_2Zr(CH_2Ph)(CH_3CN)^+$ and several other highly electron-deficient, early-transition-metal benzyl complexes.[4,18] The acute Zr–C7–C1 angle (84.4 (5)°) and short Zr–C1 distance (2.627 (9) Å) establish that the Ph group is acting as a weak donor to the cationic Zr(IV) center. The η^2-CH_2Ph ligand is bonded in an "endo" fashion; i.e., the Ph group occupies the center coordination site. Both electronic and steric factors may contribute to the difference in benzyl ligation mode between **2** and **4**. The metal center in neutral **2** is less Lewis acidic than that in cationic **4**, and η^2 bonding in the former compound would result in steric crowding due to the presence of the second bulky benzyl ligand. The Zr–CH_2Ph bond length of **4** (Zr–C7 = 2.321 Å) is identical with that of **2**.

While the Zr–C_5 centroid distances and the centroid–Zr–Centroid angle of **4** are identical with those of **2**, the conformation of the ethylenebis(tetrahydroindenyl) ligand is quite different. In **4** the C_5 rings are rotated relative to those in **2** to a conformation in which the $(CH_2)_4$ rings point toward the sides of the metallocene structure rather than over the equatorial coordination sites as in **2**. This difference is most easily seen by comparing Figures 1b and 2b. This conformational change also twists the CH_2CH_2 bridge of **4** to a direction opposite to that in **2**. Brintzinger and co-workers have observed a similar structure for one of the diastereomers of (EBTHI)Ti(*O*-acetyl-(*R*)-mandelate)$_2$.[9c] The difference in the conformations of the ethylenebis(tetrahydroindenyl) ligands of **2** ("$(CH_2)_4$-front") and **4** ("$(CH_2)_4$-side") is related to the difference in benzyl ligation mode. In **2**, the η^1-benzyl ligands are rotated (about the Zr–CH_2Ph bonds) to conformations in which the Ph groups point away from the $(CH_2)_4$ rings of the (EBTHI)Zr framework to minimize steric crowding (Figure 1a). In contrast, in **4** the η^2-benzyl ligation restricts such rotation and steric crowding between the Ph group and one of the $(CH_2)_4$ rings would be severe without distortion of the (EBTHI)Zr ligand to place the $(CH_2)_4$ ring in the "side" position. In both complexes there are close H–H contacts between the ZrCH_2Ph hydrogens and the α-CH_2 hydrogens of the C_4 ring.[19] The "$(CH_2)_4$-side"

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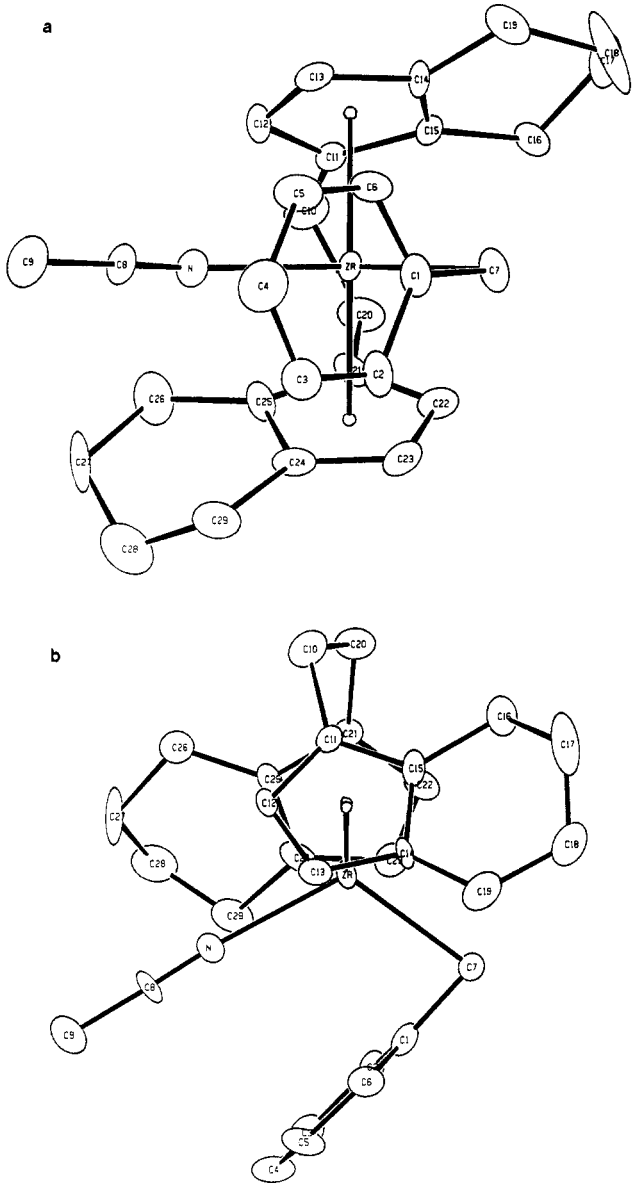


Figure 2. Molecular structure and numbering scheme of the (EBTHI)Zr(CH_2Ph)(CH_3CN)$^+$ cation of **4**: (a) front view; (b) view perpendicular to the N–Zr–Bz plane.

Table III. Positional Parameters for (EBTHI)Zr(CH_2Ph)$_2$ (2)

atom	*x*	*y*	*z*	*B*,[a] Å^2
Zr	0.000	0.26099 (3)	0.250	3.117 (7)
C1	0.1920 (3)	0.1075 (2)	0.1582 (2)	3.59 (7)
C2	0.1121 (4)	0.0357 (3)	0.1351 (3)	4.55 (9)
C3	0.1371 (4)	−0.0089 (3)	0.0678 (3)	5.3 (1)
C4	0.2420 (5)	0.0141 (3)	0.0226 (3)	5.3 (1)
C5	0.3228 (4)	0.0846 (3)	0.0443 (3)	5.2 (1)
C6	0.2984 (4)	0.1301 (3)	0.1119 (3)	4.56 (9)
C7	0.1671 (3)	0.1562 (3)	0.2302 (2)	4.17 (9)
C8	0.0512 (4)	0.3996 (3)	0.3246 (3)	4.07 (8)
C9	−0.0604 (4)	0.3589 (3)	0.3567 (2)	4.44 (8)
C10	−0.0191 (5)	0.2795 (3)	0.3923 (2)	5.5 (1)
C11	0.1212 (4)	0.2709 (3)	0.3806 (2)	4.43 (8)
C12	0.2189 (6)	0.2061 (3)	0.4167 (3)	7.9 (1)
C13	0.3564 (6)	0.2400 (7)	0.4111 (4)	13.6 (2)
C14	0.3927 (5)	0.3013 (5)	0.3614 (8)	16.4 (4)
C15	0.3056 (4)	0.3651 (4)	0.3225 (3)	6.1 (1)
C16	0.1618 (3)	0.3446 (3)	0.3381 (2)	3.74 (7)
C17	0.0541 (4)	0.4874 (3)	0.2798 (3)	5.7 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table IV. Positional Parameters for [(EBTHI)Zr(CH_2Ph)(CH_3CN)][BPh_4]•CH_3CN (4•CH_3CN)

atom	*x*	*y*	*z*	*B*,[a] Å^2
Zr	0.07764 (6)	0.21601 (6)	0.13287 (5)	2.38 (2)
N	−0.0612 (5)	0.2437 (5)	0.2655 (4)	3.1 (2)
C1	0.2252 (6)	0.1932 (6)	0.2225 (5)	3.3 (2)
C2	0.1824 (6)	0.3031 (6)	0.2609 (5)	3.7 (2)
C3	0.1246 (7)	0.3185 (7)	0.3469 (5)	4.2 (2)
C4	0.1097 (8)	0.2282 (7)	0.3987 (5)	4.8 (2)
C5	0.1515 (7)	0.1209 (7)	0.3629 (5)	4.2 (2)
C6	0.2079 (7)	0.1023 (6)	0.2752 (5)	3.8 (2)
C7	0.2780 (6)	0.1775 (6)	0.1294 (5)	3.9 (2)
C8	−0.1249 (7)	0.2533 (6)	0.3318 (5)	3.6 (2)
C9	−0.2091 (8)	0.2662 (8)	0.4170 (6)	5.5 (3)
C10	−0.0649 (7)	0.1902 (6)	−0.0100 (5)	4.0 (2)
C11	0.0100 (6)	0.1172 (6)	0.0437 (4)	2.4 (2)
C12	−0.0331 (6)	0.0904 (6)	0.1290 (5)	3.0 (2)
C13	0.0653 (6)	0.0193 (6)	0.1555 (5)	2.9 (2)
C14	0.1708 (6)	0.0020 (6)	0.0875 (5)	3.0 (2)
C15	0.1370 (6)	0.0644 (6)	0.0186 (5)	3.0 (2)
C16	0.2249 (7)	0.0555 (7)	−0.0716 (6)	4.3 (2)
C17	0.3331 (9)	−0.0510 (9)	−0.0846 (8)	7.4 (4)
C18	0.3834 (8)	−0.073 (1)	−0.0142 (7)	9.7 (4)
C19	0.2964 (7)	−0.0833 (7)	0.0736 (6)	4.7 (3)
C20	−0.0237 (7)	0.2927 (6)	−0.0446 (5)	4.0 (2)
C21	0.0012 (6)	0.3438 (6)	0.0241 (5)	2.8 (2)
C22	0.1149 (7)	0.3518 (6)	0.0190 (5)	3.4 (2)
C23	0.1026 (7)	0.4086 (6)	0.0908 (5)	3.5 (2)
C24	−0.0189 (7)	0.4364 (6)	0.1426 (5)	3.1 (2)
C25	−0.0822 (7)	0.3930 (6)	0.1031 (5)	3.0 (2)
C26	−0.2179 (8)	0.4208 (8)	0.1334 (6)	4.9 (3)
C27	−0.2778 (8)	0.4898 (8)	0.2170 (8)	6.4 (3)
C28	−0.219 (1)	0.5676 (9)	0.2280 (6)	7.3 (3)
C29	−0.0849 (8)	0.5097 (7)	0.2222 (6)	4.8 (3)
C30	0.564 (1)	0.825 (1)	0.6456 (9)	9.9 (4)*
C31	0.438 (1)	0.836 (1)	0.671 (1)	10.7 (4)*
N2	0.339 (1)	0.836 (1)	0.701 (1)	14.3 (4)*
B	0.7167 (8)	0.3578 (7)	0.6874 (6)	3.0 (2)*
C1P	0.8572 (7)	0.2672 (6)	0.6702 (5)	3.8 (2)*
C2P	0.8960 (7)	0.1596 (7)	0.6339 (5)	4.3 (2)*
C3P	1.0197 (8)	0.0853 (8)	0.6143 (6)	5.6 (2)*
C4P	1.1010 (8)	0.1170 (8)	0.6340 (6)	5.8 (2)*
C5P	1.0675 (9)	0.2222 (8)	0.6710 (7)	6.3 (3)*
C6P	0.9465 (8)	0.2958 (7)	0.6879 (6)	5.2 (2)*
C11P	0.7107 (6)	0.4410 (6)	0.6042 (5)	3.1 (2)*
C12P	0.8151 (7)	0.4659 (6)	0.5517 (5)	3.9 (2)*
C13P	0.8086 (7)	0.5429 (7)	0.4868 (6)	4.7 (2)*
C14P	0.7029 (8)	0.5974 (7)	0.4695 (6)	4.8 (2)*
C15P	0.5988 (8)	0.5728 (7)	0.5174 (6)	4.9 (2)*
C16P	0.6038 (7)	0.4969 (6)	0.5838 (5)	3.6 (2)*
C21P	0.6202 (7)	0.2859 (6)	0.7036 (5)	3.6 (2)*
C22P	0.6049 (7)	0.2408 (7)	0.6364 (6)	4.7 (2)*
C23P	0.5287 (9)	0.1738 (8)	0.6492 (7)	6.2 (3)*
C24P	0.4677 (8)	0.1516 (7)	0.7299 (6)	5.4 (2)*
C25P	0.4829 (8)	0.1926 (7)	0.7961 (6)	5.0 (2)*
C26P	0.5571 (7)	0.2604 (6)	0.7837 (5)	3.8 (2)*
C31P	0.6709 (6)	0.4396 (6)	0.7724 (5)	3.1 (2)*
C32P	0.5890 (7)	0.5491 (7)	0.7790 (6)	4.5 (2)*
C33P	0.5430 (8)	0.6185 (7)	0.8542 (6)	4.8 (2)*
C34P	0.5802 (8)	0.5735 (7)	0.9208 (6)	4.9 (2)*
C35P	0.6602 (8)	0.4679 (7)	0.9181 (6)	5.1 (2)*
C36P	0.7086 (7)	0.4008 (6)	0.8437 (5)	3.8 (2)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as in footnote *a* of Table III.

conformation of the (EBTHI)Zr framework might be expected in other complexes containing ligands that are bulky both above and below the "equatorial" plane.

Solution Structures and Reactivity of 2 and 4. The ^1H and ^{13}C NMR spectra of **2** (Table V)[20,21] establish that

(19) For **2**, H7A–H12A = 2.33 Å. For **4**, H7A–H19B = 2.03 Å and H6–H19B = 2.41 Å.

(20) Assignments in Table I were made with the aid of decoupling experiments and data for related complexes,[4,5] including partially deuterated compounds.[21]

Table V. ^1H and ^{13}C NMR Data[a]

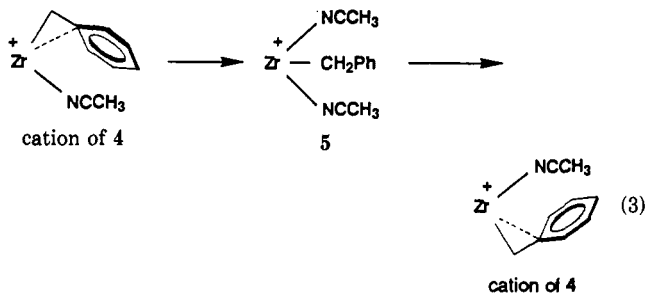
compd [solvent]	^1H NMR	assignt	^{13}C NMR	assignt
(EBTHI)Zr(CH_2Ph)$_2$ (2) [C_6D_6]	7.27 (t, J = 7.1, 4 H)	Ar*H* (meta)	154.4	Ar ipso
	7.05 (d, J = 7.5, 4 H)	Ar*H* (ortho)	128.6	Ar
	6.94 (t, J = 7.4, 2 H)	Ar*H* (para)	128.1	C_5 ipso[b]
	5.37 (d, J = 3.0, 2 H)	C_5H_2	125.5	C_5 ipso
	5.08 (d, J = 3.0, 2 H)	C_5H_2	125.4	C_5 ipso
	2.5–2.0 (m, 12 H)	CH_2CH_2 (bridge)	122.5	Ar
		$CH_2CH_2CH_2CH_2$	121.0	Ar
	1.89 (d, J = 11.2, 2 H)	CH_2Ar	115.2	C_5
	1.49 (d, J = 11.2, 2 H)	CH_2Ar	108.3	C_5
	1.7–1.2 (m, 8 H)	$CH_2CH_2CH_2CH_2$	66.5	CH_2Ar
			28.1	CH_2CH_2 (bridge)
			24.1	C_6
			23.5	C_6
			23.2	C_6
			23.0	C_6
[(EBTHI)Zr(CH_2Ph)(CD_3CN)][BPh_4][c-e] (4-d_3) [CD_3CN]	7.55–7.35 (m, 11 H)	Ar*H* (para)	164.1 (q, J_{BC} = 49)	BPh_4 ipso
		$B(C_6H_5)_4$ (ortho)	137.0	BPh_4 meta
		Ar*H* (meta)	132.0	Ar or C_5 ipso
	7.13 (t, J = 7.5, 8 H)	$B(C_6H_5)_4$ (meta)	131.6	Ar or C_5 ipso
	7.00 (t, J = 7.2, 4 H)	$B(C_6H_5)_4$ (para)	131.5	Ar or C_5 ipso
	6.70 (d, J = 7.4, 2 H)	Ar*H* (ortho)	130.9	Ar or C_5 ipso
	5.75 (d, J = 2.5, 2 H)	C_5H_2	129.7	Ar or C_5 ipso
	5.62 (d, J = 3.0, 2 H)	C_5H_2	126.6 (q, J_{BC} = 3)	BPh_4 ortho
	3.25 (d, J = 7.2, 1 H)	CH_2Ar	126.1	Ar ipso
	3.15 (m, 2 H)	CH_2CH_2 (bridge)	122.9	BPh_4 para
	2.95 (m, 2 H)	CH_2CH_2 (bridge)	120.5	C_5 ipso
	2.85–2.30 (m, 8 H)	$CH_2CH_2CH_2CH_2$	110 (br)	C_5
	2.04 (d, J = 7.1, 1 H)	CH_2Ar	107.7	C_5
	1.76 (m, 8 H)	$CH_2CH_2CH_2CH_2$	51.1	CH_2Ar
			30.1	CH_2CH_2 (bridge)
			25.5	C_6
			24.6	C_6
			23.4	C_6
			23.2	C_6

[a] All shifts are in ppm and all J values in Hz. [b] From spectrum in toluene-d_8. [c] Prepared by dissolution of 3 in CD_3CN; spectra contain resonances for free THF. [d] ^1H spectrum at 50 °C. [e] ^{13}C spectrum with added $Cr(acac)_3$.

the C_2 symmetry observed in the solid state is maintained in solution. The ^1H NMR spectrum exhibits a single pattern for the Ph rings, a pair of doublets for the unsubstituted C_5 ring hydrogens, and a pair of doublets for the ZrCH_2Ph hydrogens. Thus, the halves of the ethylenebis(tetrahydroindenyl) ligand and the two benzyl ligands are equivalent. The ^1H NMR shift of the Ph ortho hydrogens and the ^{13}C shifts of the methylene and ipso carbons are in the range expected for normal, undistorted η^1-benzyl ligands.[4,18g]

The ^1H NMR spectrum of 3 in THF-d_8 solvent at ambient temperature (see Experimental Section) exhibits four doublets for the C_5 ring hydrogens, indicating the absence of a C_2 symmetry axis. Evidently exchange of coordinated and free THF is slow on the NMR time scale under these conditions. The Ph resonances appear in the normal range for undistorted η^1-benzyl ligands. Detailed assignments of the aliphatic resonances were not possible due to interference by solvent resonances and the complexity of the spectra. However, it was possible to avoid these problems by studying 3 in CD_3CN solution, in which the CD_3CN adduct 4-d_3 is formed.

The ^{13}C NMR spectrum of 4-d_3 (generated by dissolution of 3 in CD_3CN) exhibits five C_5 resonances and a single bridge CH_2 resonance, indicating that the halves of the ethylenebis(tetrahydroindenyl) ligand are equivalent. One of the *C*–H resonances of the C_5 rings is broadened at ambient temperature and sharpens as the temperature is raised. These observations are consistent with rapid (^{13}C NMR time scale) exchange of the CD_3CN and the benzyl ligand, which results in effective C_2 symmetry for the (EBTHI)Zr frame. Single resonances are observed for the o, m, and p carbons of the Ph ring, indicating that rotation about the ZrCH_2–Ph bond is rapid. An exchange process that accommodates these observations and involves an intermediate η^1-CH_2Ph species is shown in eq 3. Note that



cation of 4 5 cation of 4 (3)

simple endo/exo exchange, i.e. isomerization to place the Zr–CH_2 bond in the central coordination site, would not render the halves of the ethylenebis(tetrahydroindenyl) ligand equivalent. The ^1H NMR spectrum of 4-d_3 in CD_3CN at 25 °C is complex and contains several broad resonances which indicate that CD_3CN/benzyl exchange is occurring at an intermediate rate (on the ^1H NMR time scale). However, the 50 °C spectrum is simple and fully consistent with the ^{13}C results; i.e., two sharp doublets for the C_5 ring hydrogens are observed, consistent with fast CD_3CN/benzyl exchange and effective C_2 symmetry. Note that the ZrCH_2Ph hydrogens remain inequivalent during this proposed exchange process. Consistent with this requirement, two doublets are observed for this group, even at high temperature. The high-field ^1H shift of the ortho hydrogens and the high-field ^{13}C shifts of the ipso and

(21) Waymouth, R. M.; Bangerter, F.; Pino, P. *Inorg. Chem.* **1988**, *27*, 758.

Table VI. Summary of Crystallographic Data for (EBTHI)Zr(CH_2Ph)$_2$ (2) and [(EBTHI)Zr(CH_2Ph)(CH_3CN)][BPh_4]•CH_3CN (4•CH_3CN)[a]

compd	2	4·CH_3CN
empirical formula	$C_{34}H_{38}Zr$	$C_{57}H_{54}BNZr·C_2H_3N$
fw	537.91	896.19
cryst size, mm	0.15 × 0.25 × 0.55	cryst 1, 0.15 × 0.30 × 0.40; cryst 2, 0.10 × 0.25 × 0.30
cryst color	amber	yellow
T, K	295	295
space group	*Pbcn*	$P\bar{1}$
a, Å	10.008 (3)	12.300 (2)
b, Å	14.895 (4)	12.493 (2)
c, Å	17.532 (6)	16.633 (3)
α, deg		84.61 (1)
β, deg		71.18 (1)
γ, deg		69.42 (1)
V, Å^3	2613.5 (2.4)	2264.1 (9)
Z	4	2
d(calcd), g/cm^3	1.367	1.314
cell dimens	15 rflns, 25–30° (2θ)	25 rflns, 30–40° (2θ)
radiation	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
scan ratio, $2\theta/\omega$	1.3	1.3
scan limit, deg	$2 \le 2\theta \le 50$	cryst 1, $2 \le 2\theta \le 40$; cryst 2, $2 \le 2\theta < 30$
scan speed, deg min^{-1}	0.6–5.5	0.6–4.0
scan range	0.8 + 0.35 tan θ	0.8 + 0.35 tan θ
data collected	$-h,\pm k,\pm l$	cryst 1, $\pm h\pm k, -l$; cryst 2, $\pm h,\pm k,+l$
no. of rflns collected	10160	8291
no. of unique intens	2630	4208
decay (max cor on F)	1.032	cryst 1, 1.26; cryst 2, 1.005
agrmnt btwn edquiv rflns	4.4% on F	5.4% on F
μ, cm^{-1}	4.3	2.7
abs cor (emp on F^2)	max 1.00, min 0.84	max 1.00, min 0.77
structure soln	Patterson and DIRDIF	Patterson and DIRDIF
refinement	anisotropic on non-H	anisotropic on all non-H in cation, isotropic in anion
data/param in LS	1235/159	2440/392
R	0.032	0.050
R_w	0.035	0.062
weight (Killean and Lawrence)	P = 0.0, Q = 0.0	P = 0.04, Q = 1.0
SDOUW	1.149	0.90
max param shift/esd	0.04	0.22
max resid e density, e Å^{-3}	0.33	0.45

[a] $R = \sum\Delta F_H/\sum F_{o,H}$, where $H = hkl$, F_o is scaled to F_c, and ΔF is $||F_o| - |F_c||$. $[R_w]^2 = \sum w(\Delta F_H)^2/\sum w(F_{o,H})^2$. Killean and Lawrence weights are equal to $1/(S^2 + (PF)^2 + Q)$, where S is the esd in F from counting statistics. If several octants are averaged, S is the larger of two estimates—one based on counting statistics, the other based on the agreement between equivalent reflections. esd = estimated standard deviation. (Killean, R. C. G.; Lawrence, J. L. *Acta Crystallogr.* **1969**, *B25*, 1750.) SDOUW = standard deviation in an observation of unit weight.

methylene carbons establish that the predominant species in solution has an η^2-CH_2Ph structure, as assumed in the foregoing discussion.[4,18g]

Complex **3** catalyzes the polymerization of ethylene in CH_2Cl_2 solvent under mild conditions (25 °C, 1 atm). However, no reaction with propylene is observed under these conditions. Presumably, this is due to the presence of the THF ligand, which inhibits coordination of the propylene. Attempts to polymerize propylene by generating the base-free complex (EBTHI)Zr(CH_2Ph)$^+$ in situ (by reaction of **2** with [($C_5H_4Me)_2Fe$][BPh_4] under 1 atm of propylene) were unsuccessful. There is also no evidence for CH_3CN insertion of **4** even at elevated temperatures. We have shown in related ($C_5H_5)_2Zr$ and ($C_5H_4Me)_2Zr$ systems that such insertions proceed for the mono(acetonitrile) complexes Cp′$_2$Zr(CH_3CN)(R)$^+$ but not the bis(acetonitrile) complexes Cp′$_2$Zr($CH_3CN)_2$(R)$^+$, with which they are in equilibrium.[16b] The lack of CH_3CN insertion for **4** (and for related η^2-CH_2Ph complexes)[4,16b] is likely due to the fact that the coordinated CH_3CN is not cis to the Zr–CH_2 bond, which must migrate for insertion to occur.

Comparison with Related Complexes. It has been shown previously that the presence of a link connecting the Cp ligands can dramatically alter the behavior of metallocene derivatives due to differences in the Cp–M–Cp angle that affect steric properties, differences in the accessibility of the Cp hydrogens, differences in ligand rigidity, and other effects. For example, for d^0 Cp_2M^{IV} complexes, one-electron reduction potentials and reactivity with H_2 and with olefins are very sensitive to the presence of bridging groups between the Cp ligands.[2e,11c,22] In the present work, however, the structures and reactivity of **2–4** parallel those observed previously for the analogous Cp_2Zr and ($C_5H_4Me)_2Zr$ complexes.[4,16b] We are currently exploring applications of **2–4** in the C–C bond-forming reactions developed for the Cp_2Zr and ($C_5H_4Me)_2Zr$ analogues.[5,6]

Implications for Olefin Polymerization. Complexes **2–4** are models for the (EBTHI)Zr(R)(olefin)$^+$ species, which are believed to play a key role in isospecific propene polymerization catalysts based on **1**.[11,12] The orientation of the Ph groups in **2** clearly shows that the (EBTHI)Zr frame strongly influences the orientation of ligands in the equatorial plane and that structures with the large groups pointed away from the ($CH_2)_4$ rings are favored. In both **2** and **4** the key steric interactions are between the α-CH_2 (C12 in **2**, C19 and C29 in **4**) and the equatorial ligands.

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Recent theoretical and experimental studies of isospecific propene polymerization by catalysts based on **1** suggest that such steric interactions largely determine the structures of the putative (EBTHI)Zr(propene){$CH_2CH(Me)$-(R)}$^+$ intermediates and the stereochemistry of propene insertion.[2e,9,11,12,23]

The observation of the "$(CH_2)_4$-front" structure for **2** and the "$(CH_2)_4$-side" structure for **4** and the thermal ellipsoids for the $(CH_2)_4$ carbons in **2** and **4** show that the (EBTHI)Zr framework is somewhat flexible and can adopt different conformations depending on the steric requirements of the equatorial ligands. In particular the "$(CH_2)_4$-side" structure of **4** and (EBTHI)Ti(*O*-acetyl-(*R*)-mandelate)$_2$ is expected for complexes which contain ligands that are bulky both above and below the equatorial plane between the Cp ligands. We recently discovered that $(C_5H_4Me)_2Zr(CH_2CH_2R)(L)^+$ complexes adopt β-agostic structures when L is a two-electron donor such as PMe_3 or CH_3CN.[6f,16b] It is likely that similar agostic interactions would be present in the (EBTHI)Zr(CH_2CHMeR)(propene)$^+$ (R = growing polymer) ions and that, on the basis of the foregoing discussion, the "$(CH_2)_4$-side" conformation would be preferred for such species.

Experimental Section

General Considerations. All manipulations were performed under an inert atmosphere or under vacuum with use of a Vacuum Atmospheres drybox or a high-vacuum line. Solvents were purified by initial distillation from an appropriate drying/deoxygenating agent followed by vacuum transfer from the same.[24] NMR spectra were obtained on Bruker WP-360 or MSL-300 instruments. ^1H and ^{13}C chemical shifts are reported vs Me_4Si and were determined by reference to the residual ^1H or ^{13}C solvent peaks. Elemental analyses were performed by Analytische Laboratorien, Gummersbach, West Germany. $Na[BPh_4]$, $(C_5H_4Me)_2Fe$, and ^nBuLi (hexane solution) were purchased from Aldrich and used as supplied. K[O^{t}Bu] was purchased from Aldrich and sublimed under vacuum (1×10^{-3} Torr, 130 °C) prior to use. $K[CH_2Ph]$[25] and $[(C_5H_4Me)_2Fe][BPh_4]$[6e] were prepared according to literature procedures. (EBTHI)$ZrCl_2$ was supplied by Dr. J. A. Ewen.

(EBTHI)Zr(CH_2Ph)$_2$ (2). A 100-mL flask was charged with 2.510 g (5.89 mmol) (EBTHI)$ZrCl_2$ and 1.535 g (11.79 mmol) of $K[CH_2Ph]$. THF (50 mL) was added by vacuum transfer at −78 °C. The solution was warmed to 0 °C, stirred for 1.5 h, and filtered to yield a yellow solid and a reddish brown solution. The solid was placed in a continuous Soxhlet-type extraction apparatus and extracted with 100 mL of toluene for 24 h. The toluene slurry of the product obtained from this extraction was concentrated to ca. 40 mL, and the yellow solid was collected by filtration. After it was washed with two 5-mL portions of toluene, the product was vacuum-dried overnight. An additional extraction of this solid was necessary to obtain analytically pure material; yield 2.333 g (73.7%). Anal. Calcd for $C_{34}H_{38}Zr$: C, 75.92; H, 7.12; Zr, 16.96. Found: C, 75.91; H, 6.92; Zr, 16.82.

[(EBTHI)Zr(CH_2Ph)(THF)][BPh_4] (3). A 50-mL flask was charged with 0.540 g of **2** (1.00 mmol) and 0.602 g of $[(C_5H_4Me)_2Fe][BPh_4]$ (1.13 mmol). THF (30 mL) was added by vacuum transfer at −78 °C, and the mixture was warmed to room temperature and stirred for 30 min. During this period the reaction mixture changed from a blue-green slurry to an orange solution. The solution was concentrated to ca. 25 mL, and a small amount of colorless solid was removed by filtration. The volume was further reduced to ca. 10 mL, and 10 mL of toluene was added at −78 °C. Removal of the solvent under vacuum produced a red-orange oil, which was washed with two 5-mL portions of toluene and dried. THF (10 mL) was added to the oil, and the mixture was warmed to room temperature with stirring to produce an orange slurry. The orange solid was isolated by filtration, washed with two 5-mL portions of THF, and vacuum-dried overnight; yield 0.637 g (76.0%). ^1H NMR (THF-d_8): δ 7.30 (m, 8 H, BPh_4^- ortho), 7.21 (t, J = 7.2 Hz, 2 H, Ph meta), 6.92 (m, 3 H, Ph ortho and para), 6.87 (t, J = 7.2 Hz, 8 H, BPh_4^- meta), 6.72 (t, J = 7.2 Hz, 4 H, BPh_4^- para), 6.04 (d, J = 2.9 Hz, 1 H, C_5H_2), 6.00 (d, J = 2.8 Hz, 1 H, C_5H_2), 5.53 (d, J = 2.9 Hz, 1 H, C_5H_2), 5.42 (d, J = 2.8 Hz, 1 H, C_5H_2), 3.40 (m, 1 H), 3.04 (d, J = 11.8 Hz, 1 H, $ZrCH_2Ph$), 3.00–2.65 (m, 9 H), 2.4 (m, 1 H), 2.1–1.5 (m, integration precluded by interference from solvent peak), 1.40 (m, 1 H), 1.30 (d, J = 11.8 Hz, 1 H, $ZrCH_2Ph$). Anal. Calcd for $C_{55}H_{59}BOZr$: C, 78.82; H, 7.10; Zr, 10.89. Found: C, 78.58; H, 7.00; Zr, 10.72.

X-ray Structure Determinations of 2 and 4. Crystallographic data for **2** and **4** are summarized in Table VI. Suitable crystals of **2** were grown by slow cooling of a benzene solution. Suitable crystals of **4**, which contain 1 equiv of CH_3CN in the lattice, were grown by slow cooling of a CH_3CN solution. Intensity data were collected at 25 °C with an Enraf-Nonius CAD-4 diffractometer system, and the crystallographic calculations were performed by using the SDP package for that system.[26] For **2**, the large thermal ellipsoids for C12, C13, and C14 indicate some disorder in the C_4 ring of the ethylenebis(tetrahydroindenyl) ligand. Attempts to use a disordered model with two limiting disordered conformations were unsuccessful. The shapes of the ellipsoids indicate the direction of the conformational variations, and the excellent fit of the model to the data may indicate that this complex exists in a range of conformations rather than in two limiting conformations. For **4**, data sets were collected for two crystals and merged.

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Supplementary Material Available: Tables of hydrogen atom positional parameters and anisotropic thermal parameters for **2** and **4** (5 pages); listings of h, k, l, F_o, F_c, and $\sigma(F_o)$ (14 pages). Ordering information is given on any current masthead page.

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