Synthesis and Structural Investigation of Stable Zirconacyclopentanes Which Bear Additional Functional Groups

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The reactions of zirconocene-alkyne complexes $Cp'_2Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ {$Cp'_2 = (\eta^5\text{-}C_5H_5)_2$: L = THF, **1**; L = pyridine, **2**; Cp'_2 = *rac*-ebthi, **3**, [ebthi = 1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)]} with 2 equiv (or excess) of bicyclo[2.2.1]hepta-2,5-diene (NBD) in THF at 50 °C result in five-membered zirconacyclopentane complexes $Cp_2Zr(C_{14}H_{16})$ (**4**) and *rac*-(ebthi)$Zr(C_{14}H_{16})$ (**5**) ($C_{14}H_{16}$ means two coupled NBDs) in good yields. NMR spectra of complexes **4** and **5** show the C_2 symmetry of the molecules, indicating that the two NBD components in the complexes are in *exo*−*trans*−*exo* conformation. An X-ray crystallographic structure determination of **5** confirms that the two NBD fragments are *exo*−*trans*−*exo* linked to form a racemate. Both optical isomers are present in a 1:1 ratio in the crystals. Reactions of **1** and **2** with 1 equiv of NBD have also been investigated, and only zirconacyclopentane complex **4** was isolated from the reactions. The analogous zirconacyclopentane complexes $Cp_2Zr(C_{22}H_{20})$ (**6**) and *rac*-(ebthi)$Zr(C_{22}H_{20})$ (**7**) ($C_{22}H_{20}$ means two coupled BNBDs) are obtained from the reactions of **1** (or **2**) and **3** with an excess of 1,4-dihydro-1,4-methanonaphthalene (BNBD), respectively. The X-ray structure of the orange complex **7** shows that the geometry of the Zr coordination sphere can be described as a distorted tetrahedron and similar to that of **5**. The zirconacyclopentane complex *rac*-(ebthi)$Zr(C_{14}H_{15}N)$ (**9**), bearing a free N coordinating site and a double bond, is formed from the coupling reaction of *rac*-(ebthi)$Zr(C_7H_7N)$ (**8**) with NBD. All these reactions are stereospecific, and all new complexes are characterized by NMR, MS, and elemental analysis.

Introduction

Five-membered zirconacycles have attracted considerable interest, as such complexes are considered to be the intermediates of catalytic processes in coupling reactions of unsaturated hydrocarbons.[1] However, only a small number of zirconacycles have been isolated and structurally characterized, and moreover, most of them are zirconacyclopentadienes. To the best of our knowledge, only a few zirconacyclopentanes[2] have been structurally characterized so far. In general, the stability decreases from zirconacyclopentadienes to zirconacyclopentenes to zirconacyclopentanes.

We have been interested in the chemistry of titanocenes and zirconocenes for years.[3] Previous work[4] done in this laboratory on the reactions of *rac*-(ebthi)-$Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$[5] [ebthi = 1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)] with ethylene or styrene has shown that the bis(trimethylsilyl)acetylene ligand is reluctant to undergo coupling reactions. Another example of a zirconacyclopentane compound is $Cp_2Zr(C_9H_{11}N)$,[6] which was obtained from the reaction of $Cp_2Zr(C_7H_7N)$ (C_7H_7N means "2-vinylpyridine") with ethylene. The work by Catellani[7] on aromatic arylation has shown that palladacycles that were regarded as metal-catalyzed transformation intermediates were formed through insertion of norbornene into the phenylpalladium bond. These works prompted us to extend our investigations and explore new zirconacyclopentanes that bear additional functional groups. Another impetus for this study comes from the idea of applying molecular architect method-

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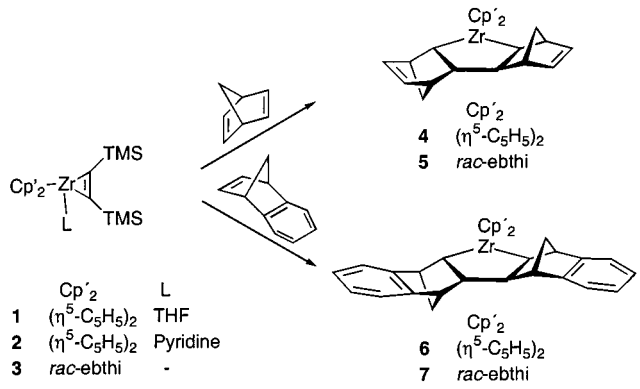
Scheme 1



ologies[8] that were used in organic chemistry to organometallic compounds. The latter is the subject of one of our long-term goals.

Results and Discussions

Synthesis of the Compounds. Zirconocene-alkyne complexes $Cp'_2Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ [Cp'_2 = (η^5-$C_5H_5)_2$: L = THF,[9] **1**; L = pyridine,[10] **2**; Cp'_2 = *rac*-ebthi,[5] **3**] reacted with 2 equiv (or excess) of bicyclo[2.2.1]hepta-2,5-diene (NBD) in THF at 50 °C to afford, after elimination of the alkyne $Me_3SiC_2SiMe_3$, zirconacyclopentane complexes $Cp_2Zr(C_{14}H_{16})$ (**4**) and *rac*-(ebthi)$Zr(C_{14}H_{16})$ (**5**) (as shown in Scheme 1).

At room temperature the reactions were unbearably slow, but they could be sped by the use of excess NBD or at a higher temperature. The golden yellow complex **4** is sensitive toward air and moisture. It has a very high solubility even in *n*-hexane and *n*-pentane. As a result, the purification of **4** has to be done in *n*-hexane at −78 °C. Complex **5**, which is stable toward air and moisture in the solid state, is moderately soluble in benzene, toluene, and THF, but insoluble in saturated hydrocarbon solvents. Single crystals of **5** suitable for an X-ray crystal structure determination could be grown from toluene.

From the reactions of **1** and **2** with 1 equiv of NBD, after workup and crystallization, complex **4** along with "unreacted" starting materials of **1** and **2** were isolated, indicating that the isolation of 1:1 ($Me_3SiC_2SiMe_3$/NBD) coupling product from the reaction is impossible. Our previous work[4] on the formation of *rac*-[1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)zirconacyclopentane from the reaction of *rac*-(ebthi)$Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with ethylene showed that the possible intermediate zirconacyclopentene was formed in solution below 210 K (as shown in Scheme 2). But the analogous intermediates were not detected in the formation of compounds **4** and **5**. Monitoring the reactions of **1** or **2** with norbornadiene by ^{1}H NMR spectroscopy does not give clear evidence for the existence of transient zirconacylopentenes nor for the formation of other zirconacyclopentanes than **4** or **5** (stereoisomers of the *exo*−*trans*−*exo* forms, see

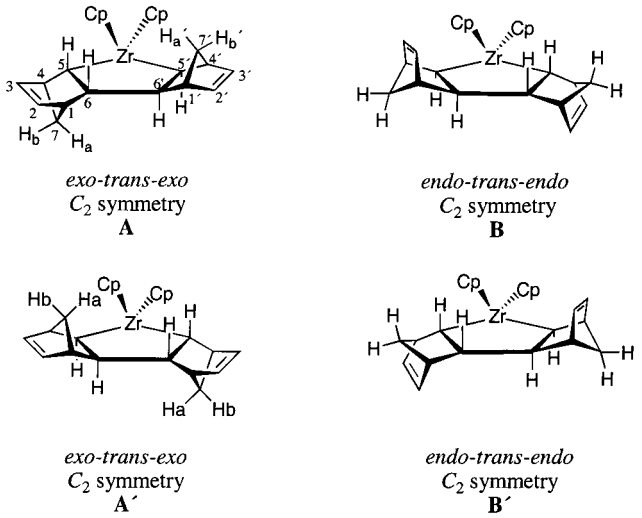


Figure 1. Isomers that possess C_2 symmetry for **4**.

discussion below). The products are stable in solution and do not undergo isomerization by cycloreversion, as it was observed for a zirconacyclopentane obtained with styrene,[6] so it is reasonable to assume a clean formation of the preferred *exo*−*trans*−*exo* isomer.

For further comparison, we have prepared the closely related zirconacyclopentane complexes $Cp_2Zr(C_{22}H_{20})$ (**6**) and *rac*-(ebthi)$Zr(C_{22}H_{20})$ (**7**) by reacting **1** (or **2**) and **3** with 1,4-dihydro-1,4-methanonaphthalene (BNBD), respectively, in a procedure similar to that described for complexes **4** and **5** (Scheme 1).

Complex **6** is sparingly soluble in saturated hydrocarbon solvents and is soluble in THF and aromatic solvents. The pure yellow solid was obtained by recrystallization from THF/hexane (1:3). The physical properties of **7** are quite similar to that of **5**. Careful recrystallization from warm toluene gives orange crystals of **7**.

The zirconacyclopentane *rac*-(ebthi)$Zr(C_{14}H_{15}N)$ (**9**) was isolated in 58% yield from the reaction of *rac*-(ebthi)$Zr(C_7H_7N)$ (**8**) and an excess of NBD (Scheme 3). "2-Vinylpyridine"[6] in complex **8** does not behave like bis(trimethylsilyl)acetylene in compound **3**. The latter is reluctant to undergo coupling reactions,[3b] while the former undergoes coupling reaction exclusively with NBD. Complex **5**, the coupling product from **3** and two NBDs, was not detected from this reaction (Scheme 3), although a large excess of NBD was used. These reactions also demonstrated the different selectivity between a "2-vinylpyridine"-containing (such as **8**) and a bis(trimethylsilyl)acetylene-containing (such as **1**, **2**, and **3**) zirconocene complex.

NMR Characterization of Zirconacyclopentane Complexes. The ^{1}H NMR spectrum of complex **4** exhibits a relatively simple pattern, eight signals for the NBD moieties together with one singlet for the cyclopentadienyl groups. The bridge protons (7-H_a, 7-H_a′ and 7-H_b, 7-H_b′ in Figure 1) appear at δ 1.68 and 1.45 ppm, respectively, as doublets with a coupling constant ^2J = 7.9 Hz. 1-H, 1-H′ and 4-H, 4-H′ appear at about 2.6 ppm without resolved couplings. The signals assigned to 6-H, 6-H′ and 5-H, 5-H′ (the former double bond) appear now in the aliphatic region (δ 1.32 and 0.74 ppm) and prove the linkage of the unsaturated hydrocarbons to a zirconacyclopentane. The olefinic protons 2-H, 2-H′ and

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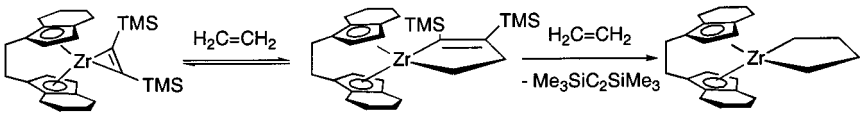
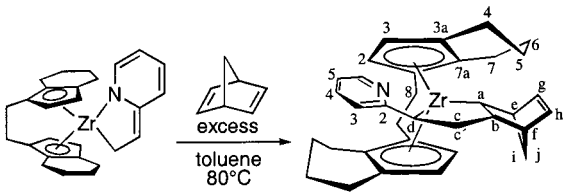
Scheme 2



Scheme 3



8 **9**

3-H, 3-H′ are found at δ 5.90 and 6.27 ppm, respectively. The ^{13}C NMR spectrum exhibits seven signals for the coupled norbornadiene moieties, and the Cp groups appear at δ 113.3 ppm. Thus the molecule must have C_2 symmetry.

There are two NBD fragments in complex **4**, and each of the NBD fragments has four possible conformations. They are, in each case, bridge carbon (C7 in Figure 1) up, bridge carbon down, NBD *exo*, NBD *endo*. Therefore, there are totally 16 possible conformations for complex **4**. The only four isomers (A, A′, B, and B′ as shown in Figure 1) of the 16 possibilities possess C_2 symmetry. Experiments[8] have shown that coupling and cycloaddition reaction products of NBD are normally in *exo* conformations. Therefore, the most probable stereochemistry of complex **4** should be *exo*−*trans*−*exo* (A) or its mirror image *exo*−*trans*−*exo* (A′), which is compatible with the observed ^{1}H NOE correlations for complex **4** and its analogue **5** (see below).

The NMR spectra of the NBD fragments in complex **5** are similar to those of **4**, in particular the ^{13}C NMR shifts. From that and the number of signals, indicating C_2 symmetry again, we have to conclude that the constitution and stereochemistry of the two complexes are analogous. Inspection of a molecular model reveals that the *exo*−*trans*−*exo* arrangement of the NBD fragments (Figure 1) is the only one avoiding steric interference with the *rac*-ebthi ligand system. This is supported by all observed ^{1}H NOE correlations, e.g., 25-H$_a$ (inward pointing) to 6-H and 22-H, 26-H to 6-H, 29-H to 27-H (numbering refers to Figure 2).

The NMR spectra of complexes **6** and **7** are comparable with each other, and both are similar to those of **4** and **5**; therefore the above discussions can also be applied to these two complexes.

The structure of complex **9** is easy to determine, because the conformation of the NBD moiety can only be in *exo* position and with its bridge carbon away from the six-membered ring. In other word, the stereoconfiguration of the "ebthi" group prevents the NBD moiety from being in the *endo* form or the bridge carbon from facing toward the six-membered ring (it is easier to see using a molecular model). The question whether the pyridyl substituent resides in the α or β position of the metallacycle can be answered by ^{1}H NMR NOE spectroscopy. There are correlation signals between 6-H of the pyridyl group and ebthi protons (8-H, ethylene bridge, and 2-H, see Scheme 3), but none are observed between pyridyl signals and signals of the NBD fragment. This means that the former is bound at the α carbon of the zirconacyclopentane and preferentially oriented with the nitrogen atom pointing toward the zirconium center, but there is no evidence for any interaction between nitrogen and zirconium. This orientation may also explain the unusual high-field shift of ebthi-3-H (δ 3.84 ppm): this proton is located perpendicular above the plane of the pyridine ring, so its shift is influenced by the magnetic anisotropy of the arene.

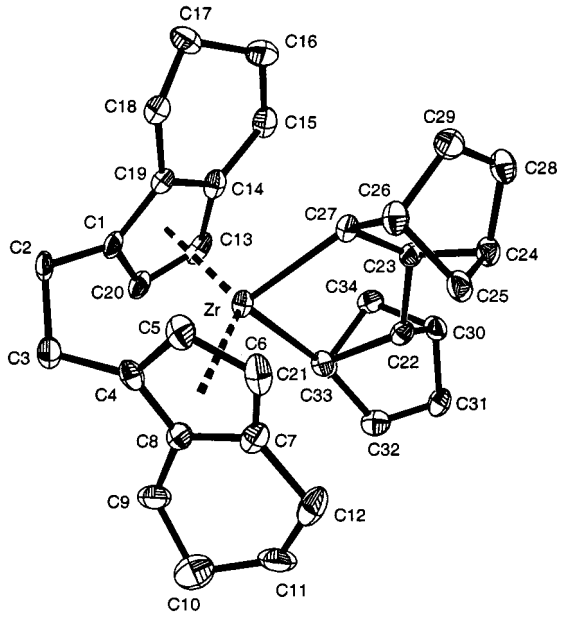


Figure 2. Molecular structure and atom-labeling scheme for *rac*-(ebthi)Zr($C_{14}H_{16}$) (**5**). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr−C21, 2.284(6); Zr−C27, 2.305(6); C21−C22, 1.572(8); C22−C23, 1.554(8); C23−C27, 1.568(8); C28−C29, 1.328(8); C26−C27, 1.557(8); C23−C24, 1.561(8); C26−C29, 1.496(8); C24−C28, 1.495(8); C24−C25, 1.547(8); C25−C26, 1.530(8); C21−Zr−C27, 87.5(2); Zr−C27−C23, 103.7(4); Zr−C21−C22, 103.8(4); C21−C22−C23, 119.1(5); C27−C23−C22, 118.8(5).

Mass Spectra of the Zirconacyclopentane Complexes. The mass spectra of the zirconacyclopentane complexes are all simple and in agreement with their compositions. Molecular ion $[M]^+$ or $[M - 1]^+$ and other main fragments, such as $[M -$ NBD (or BNDB)$]^+$ or $[M -$ 2NBD (or 2BNDB)$]^+$, are observed for complexes **4**, **5**, **6**, and **7**. Additionally, besides the molecular ion $[M]^+$ and fragment $[M -$ NBD$]^+$, $[M -$ vinylpyridine$]^+$ was also observed for complex **9**.

Structure and Bonding. Complexes **5** and **7** were investigated by X-ray crystal structure analyses. The molecular structures and selected bond lengths and angles are shown in Figures 2 and 3.

The structures of **5** and **7** are very similar except that **7** cocrystallized with half a toluene molecule. The two NBD fragments in **5** and the two BNBD fragments in **7**

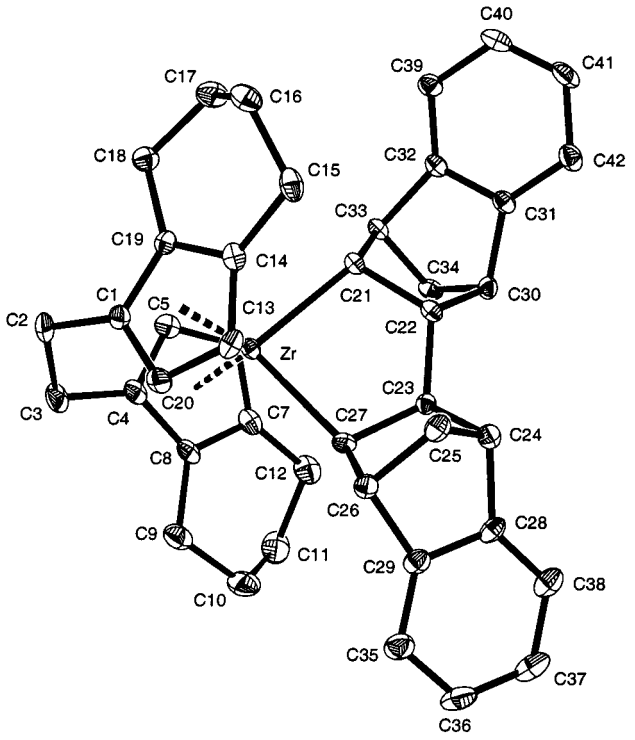


Figure 3. Molecular structure and atom-labeling scheme for *rac*-(ebthi)Zr($C_{22}H_{20}$) (**7**). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr−C21, 2.278(4); Zr−C27, 2.302(4); C21−C22, 1.582(5); C22−C23, 1.563(5); C23−C27, 1.586(6); C28−C29, 1.388(6); C26−C27, 1.550(6); C23−C24, 1.560(5); C26−C29, 1.518(5); C24−C28, 1.496(5); C24−C25, 1.550(6); C25−C26, 1.540(6); C21−Zr−C27, 87.01(1); Zr−C27−C23, 104.5(2); Zr−C21−C22, 105.4(2); C21−C22−C23, 117.5(3); C27−C23−C22, 118.6(3).

are both *exo*−*trans*−*exo* linked to form a racemate. Both optical isomers (A and A′ in Figure 1) are present in a 1:1 ratio in the crystals. The structures of the complexes in the solid state are identical with the NMR investigations in solution.

The bond lengths in the five-membered zirconacycle are comparable to those crystallographically characterized zirconacyclopentanes.[2,4] However, all intra-ring bond angles are larger than the corresponding angles normally found, e.g., C_αZr C_α 87.5(2)° in **5** and 84.0(2)° in *rac*-(ebthi)Zr(C_4H_8).[4] This means the five atoms of the ring in **5** define a "better" plane compared to those zirconacyclopentanes. This is also confirmed by the mean deviations of 0.0945 Å for **5** and 0.1630 Å for *rac*-(ebthi)Zr(C_4H_8) from the best planes defined by the five corresponding atoms of the zirconacyclopentane rings (Figure 4). The twist of the zirconacyclopentane ring is required to fulfill the demand of a tetrahedral geometry of zirconium, but the three-dimensional bulky factor of NBD fragments makes the twist of the five-membered ring much more difficult than those of less bulky fragments such as ethylene in *rac*-(ebthi)Zr(C_4H_8).

Conclusions

Zirconocene-alkyne complexes $Cp'_2Zr(L)(\eta^2$-Me_3SiC_2-$SiMe_3)$ react with olefin compounds NBD or BNDB giving exclusively olefin coupling products (**4**, **5**, **6**, and **7**). The stereochemistry of these zirconacyclopentane

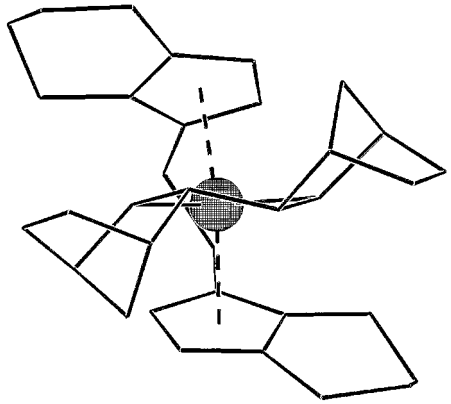


Figure 4. Perspective view of **5** parallel to the zirconacyclopentane five-membered ring.

complexes are all exclusively in *exo*−*trans*−*exo* conformation, and both optical isomers are present in the solid state as well as in solution to form a racemate. These reactions have shown the sterospecifity of "Cp'_2Zr" toward NBD and BNBD. The "ebthi"-containing zirconacyclopentane complexes (**5** and **7**) are much more stable than those of "Cp"-containing complexes (**4** and **6**). The zirconocene complex *rac*-(ebthi)Zr(C_7H_7N) reacts with the olefin NBD, giving only a coupling of "2-vinylpyridine" and NBD to the product **9**. The conclusion[3b] is once more demonstrated that η^2-$Me_3SiC_2SiMe_3$ in zirconocene complexes is reluctant to undergo coupling reactions; nevertheless, "2-vinylpyridine" in the zirconocene complex undergoes a coupling reaction exclusively. Complexes **4**, **5**, and **9** contain additional functional groups, i.e., double bond or N-coordinating site. Investigation of their reactivity is in progress.

Experimental Section

General Procedure. All manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques. All solvents were freshly distilled from sodium tetraethylaluminate under argon prior to use. Deuterated solvents were treated with sodium or sodium tetraethylaluminate, distilled, and stored under argon. Complexes **1**,[9] **2**,[10] **3**,[5] **8**,[6] and BNBD[11] were prepared as described in the literature. NMR spectra were recorded on a Bruker ARX 400 spectrometer. Data are given in ppm relative to TMS with the solvent signals as secondary standards (C_6D_6, ^{1}H, δ 7.16 ppm; ^{13}C, 128.0 ppm, THF-d_8, ^{1}H, δ 1.73 ppm; ^{13}C, 25.2 ppm). Signal assignments were confirmed by 2D shift correlation and NOE methods. Mass spectra were obtained on a AMD 402 spectrometer operating in the electron ionization mode at 70 eV. Elemental analyses were carried out with a Leco CHNS-932 elemental analyzer. Melting points were measured in sealed capillaries on a Büchi 535 apparatus.

Preparation of $Cp_2Zr(C_{14}H_{16})$ (4) from $Cp_2Zr(THF)(\eta^2$-$Me_3SiC_2SiMe_3)$ (1). NBD (0.2 mL, 1.9 mmol) was added to a solution of **1** (441 mg, 0.95 mmol) in 10 mL of THF. The mixture was stirred at 50 °C for 2 h, and the color changed from red to dark brown. The reaction was continued for another 8 h at the same condition, and a yellow-green solution was obtained. All volatiles were removed in vacuo, and the residue was extracted with *n*-hexane. The *n*-hexane solution was cooled to −78 °C, and a yellow solid was obtained. The solid was recrystallized from *n*-hexane to afford golden yellow amorphous solids. Yield: 320 mg (83%). Mp: 206−207 °C.

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Anal. Calcd for $C_{24}H_{26}Zr$: C, 71.05; H, 6.46. Found: C, 70.95; H, 6.12. ^{1}H NMR (C_6D_6, numbering refers to Figure 1): δ 0.74 (2H, m, 6-H), 1.32 (2H, m, 5-H), 1.45 (2H, d, J = 7.9 Hz, 7-H_b), 1.68 (2H, d, J = 7.9 Hz, 7-H_a), 2.60 and 2.61 (4H, 1-H and 4-H), 5.69 (10H, s, Cp), 5.90 (2H, m, 2-H), 6.27 (2H, m, 3-H). ^{13}C NMR (C_6D_6): δ 36.0 (C6), 45.5 (C7), 48.9 (C5), 50.3 (C4), 53.0 (C1), 111.3 (Cp), 130.4 (C2), 140.9 (C3). MS, *m*/*z*: 404 $[M]^+$, 312 $[M - NBD]^+$, 220 $[M - 2NBD]^+$.

Preparation of 4 from $Cp_2Zr(Py)(\eta^2$-$Me_3SiC_2SiMe_3)$ (2). A procedure similar to that described above was used in the reaction of NBD (0.15 mL, 1.4 mmol) with **2** (320 mg, 0.7 mmol) in 15 mL of THF. Yield: 188 mg (68%).

Preparation of *rac*-(ebthi)Zr($C_{14}H_{16}$) (5). To a solution of **3** (250 mg, 0.48 mmol) in 10 mL of THF was added NBD (0.12 mL, 1.1 mmol). The mixture was heated to 50 °C for 10 h with stirring, and the volatile was removed in vacuo. The solid residue was washed with cooled *n*-hexane, and an orange solid remained. After crystallization from toluene, orange stable crystals were obtained. Yield: 141 mg (55% based on **3**). Mp: 202 °C (dec). Anal. Calcd for $C_{34}H_{40}Zr$: C, 75.64; H, 7.47. Found: C, 75.56; H, 7.46. ^{1}H NMR (THF-d_8, numbering refers to Figure 2): δ 0.39 (2H, 21-H and 27-H), 0.60 (2H, 22-H and 23-H), 1.13 (2H, d, J = 7.4 Hz, 25-H_b and 34-H_b), 1.56 (2H, d, J = 7.4 Hz, 25-H_a and 34-H_a), 1.6 (8H, m, 10-H, 11-H, 16-H, and 17-H), 2.17 (2H, dt, 9-H_{inside} and 18-H_{inside}), 2.38 (2H, 24-H and 30-H), 2.39 (2H, dt, 12-H_{inside} and 15-H_{inside}), 2.55 (2H, dt, 9-$H_{outside}$ and 18-$H_{outside}$), 2.59 (2H, 26-H and 33-H), 2.71 (2H, dt, 12-$H_{outside}$ and 15-$H_{outside}$), 2.71 and 2.85 (4H, 2-H and 3-H), 5.30 (2H, d, J = 3.1 Hz, 5-H and 20-H), 5.52 (2H, dd, 28-H and 31-H), 5.98 (2H, dd, 29-H and 32-H), 6.33 (2H, d, J = 3.1 Hz, 6-H and 13-H). ^{13}C NMR (THF-d_8): δ 23.3 and 23.8 (C10, C11, C16, and C17), 23.9 (C9 and C18), 24.5 (C12 and C15), 27.5 (C2 and C3), 40.2 (C22 and C23), 46.5 (C25 and C34), 50.1 (C26 and C33), 52.6 (C21 and C27), 52.8 (C24 and C30), 106.4 (C5 and C20), 113.5 (C6 and C13), 130.1 (C28 and C31), 140.9 (C29 and C32). MS, *m*/*z*: 538 $[M]^+$, 446 $[M - NBD]^+$, 354 $[M - 2NBD]^+$.

Preparation of $Cp_2Zr(C_{22}H_{20})$ (6). Following a procedure similar to that described for **4** from 295 mg (0.64 mmol) of **1** and 0.4 mL of BNBD in a mixture of THF (5 mL) and hexane (7 mL), a yellow solid of **6** was obtained after crystallization from THF/hexane (1:3). Yield: 255 mg (79% based on **1**). Mp: 154 °C (dec). Anal. Calcd for $C_{32}H_{30}Zr$: C, 75.99: H, 5.98. Found: C, 75.75; H, 5.99. ^{1}H NMR (C_6D_6, numbering refers to Figure 1): δ 1.09 (2H, m, 6-H), 1.44 (2H, m, 5-H), 1.72 (2H, d, J = 8.7 Hz, 7-H_b), 1.89 (2H, d, J = 8.7 Hz, 7-H_a), 3.04 (2H, 4-H), 3.16 (2H, 1-H), 5.54 (10H, s, Cp), 7.12 (6H, m, arene-H), 7.38 (2H, d, arene-H). ^{13}C NMR (C_6D_6): δ 38.6 (C6), 46.8 (C7), 51.3 (C5), 52.1 (C4), 54.1 (C1), 111.4 (Cp), 118.0, 121.4, 124.8, 125.8 (arene-*C*H), 146.3 (C2), 154.3 (C3). MS, *m*/*z*: 503 $[M - 1]^+$, 362 $[M - BNBD]^+$, 220 $[M - 2BNBD]^+$.

Preparation of *rac*-(ebthi)Zr($C_{22}H_{20}$) (7). 7 was obtained following a procedure similar to that described for **5** from 200 mg (0.38 mmol) of **3** and 0.3 mL of BNBD in 10 mL of THF. Yield: 158 mg (65% based on **3**). Mp: 228 (dec) Anal. Calcd for $C_{42}H_{44}Zr \cdot 1/2(C_7H_8)$ (C_7H_8 = toluene): C, 79.47; H, 7.11. Found: C, 79.77; H, 7.50. ^{1}H NMR (C_6D_6, numbering refers to Figure 3): δ 0.67 (2H, 21-H and 27-H), 1.17 (2H, 22-H and 23-H), 1.27 (4H, m, 11-H and 16-H), 1.36 and 1.42 (2H each, m, 10-H and 17-H), 1.79 (2H, d, J = 8.4 Hz, 25-H_b and 34-H_b), 1.84 (2H, dt, J_d = 16 Hz, J_t = 6.3 Hz, 9-H_{inside} and 18-H_{inside}), 1.97 (2H, d, J = 8.5 Hz, 25-H_a and 34-H_a), 2.04 (2H, dt, J_d = 16.4 Hz, J_t = 6.2 Hz, 12-H_{inside} and 15-H_{inside}), 2.24 (2H, dt, J_d = 16 Hz, J_t = 6.4 Hz, 9-$H_{outside}$ and 18-$H_{outside}$), 2.30 (2H, dt, J_d = 16.3 Hz, J_t = 6.2 Hz, 12-$H_{outside}$ and 15-$H_{outside}$), 2.44 (4H, AA′BB′, 2-H and 3-H), 3.11 (2H, 26-H and 33-H), 3.22 (2H, 24-H and 30-H), 5.01 (2H, d, J = 3.0 Hz, 5-H and 20-H), 6.34 (2H, d, J = 3.0 Hz, 6-H and 13-H), 7.09 (2H, d, 35-H and 39-H), 7.10 (2H, t, 37-H and 41-H), 7.16 (2H, 36-H and 40-H), 7.34 (2H, d, J = 7.0 Hz, 38-H and 42-H). ^{13}C NMR (C_6D_6): δ 22.5 (C10 and C17), 22.9 (C11 and C16), 23.4 (C9 and C18), 23.8 (C12 and C15), 27.3 (C2 and C3), 42.3 (C22 and C23), 47.3 (C25 and C34), 51.7 (C26 and C33), 53.5 (C24 and C30), 55.1 (C21 and C27), 106.3 (C5 and C20), 112.6 (C6 and C13), 117.4 (C35 and C39), 121.4 (C38 and C42), 121.9 (C8 and C19), 124.5 (C37 and C41), 125.4 (C1 and C4), 125.6 (C36 and C40), 126.7 (C7 and C14), 146.2 (C28 and C31), 154.3 (C29 and C32). MS, *m*/*z*: 637 $[M - 1]^+$, 496 $[M - BNBD]^+$, 354 $[M - 2BNBD]^+$.

Preparation of *rac*-(ebthi)Zr($C_{14}H_{15}N$) (9). A deep red solution of *rac*-(ebthi)Zr(vinylpyridine) (**8**) (240 mg, 0.52 mmol) and NBD (0.2 mL, 3.8 mmol) in 10 mL of toluene was heated to 80 °C with stirring until the ^{1}H NMR signals of **8** disappeared (it took about 30 h). The final red solution was dried in vacuo. The solid residue was washed with *n*-hexane, and the remaining yellow solid was crystallized from THF/hexane (2:1), giving an orange solid. Yield: 167 mg (58% based on **8**). Mp: 114 °C (dec). Anal. Calcd for $C_{34}H_{39}NZr$: C, 73.86; H, 7.11; N, 2.53. Found: C, 73.40; H, 7.36; N, 2.49. ^{1}H NMR (C_6D_6, numbering refers to Scheme 3): δ 1.30 (1H, d, $J \approx 6$ Hz, a), 1.62 (1H, j), 1.79 (1H, d, J = 7.5 Hz, i), 1.88 and 2.24 (1H each, ebthi-4′), 2.17 and 2.50 (1H each, ebthi-4), 2.27 and 2.35 (1H each, ebthi-7), 2.37 (1H, d, c′), 2.43 (1H, d, $J \approx 9$ Hz, d), 2.48 and 2.58 (1H each, ebthi-7′), 2.58 and 2.66 (ebthi-8), 2.76 (1H, d, $J \approx 6$ Hz, b), 2.77 (1H, t, $J \approx 9$ Hz, c), 2.88 (1H, f), 3.22 (1H, e), 3.84 (1H, d, J = 2.9 Hz, ebthi-3), 4.82 (1H, d, J = 2.9 Hz, ebthi-2), 5.25 (1H, d, J = 2.6 Hz, ebthi-2′), 5.76 (1H, d, J = 2.6 Hz, ebthi-3′), 6.04 (1H, dt, J_d = 6.3 Hz, J_t = 1.0 Hz, Py-5), 6.15 (1H, dd, h), 6.40 (1H, dd, g), 6.46 (1H, d, J = 8.8 Hz, Py-3), 6.78 (1H, ddd, J_1 = 8.9 Hz, $J_2 \approx 7$ Hz, $J_3 \approx 1.5$ Hz, Py-4), 7.64 (1H, dt, J_d = 5.9 Hz, $J_t \approx 1.3$ Hz, Py-6). ^{13}C NMR (C_6D_6): 22.7, 22.7, 23.0, 23.0, 23.2, 23.4, 23.9, 24.0 (ebthi-CH_2 4-7 and 4′-7′), 27.3, 27.9 (ebthi-8 and 8′), 35.7 (c), 43.4 (a), 44.9 (i), 51.2 (e), 52.6 (f), 55.9 (b), 66.5 (d), 99.0 (ebhti-2), 103.9 (ebthi-2′), 108.3 (ebthi-3), 109.0 (Py-5), 110.0 (ebthi-3′), 115.0 (Py-3), 118.6, 118.7, 127.2 (ebthi-1, 3a, 7a), 118.7, 127.1, 129.1 (ebthi-1′, 3a′, 7a′), 133.0 (h), 135.8 (Py-4), 139.8 (g), 150.6 (Py-6), 152.9 (Py-2). MS, *m*/*z*: 551 $[M]^+$, 459 $[M - NBD]^+$, 447 $[M -$ vinylpyridine$]^+$, 79 $[pyridine]^+$, 66 $[Cp + H]^+$.

X-ray Crystallographic Study of Compounds 5 and 7. Diffraction data were collected on a STOE-IPDS diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct method (SHELXS-86[12]) and refined by full matrix least squares techniques against F^2 (SHELXL-93[13]). H21 and H27 for both compound **5** and **7** were located by difference Fourier syntheses and refined isotropically, and all other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal data for **5**: $C_{34}H_{40}Zr$, M_r = 539.88, orange prism, size 0.2 × 0.3 × 0.4 mm, orthorhombic, space group *Pbca*, a = 13.037(3) Å, b = 15.717(3) Å, c = 25.071(5) Å, V = 5137.1(2) Å^3, T = 200 K, Z = 8, ρ_{calcd} = 1.396 g cm^{-3}, μ(Mo Kα) = 4.49 cm^{-1}. F(000) = 2272, 9661 reflections were measured, 2734 were independent of symmetry, 1710 were observed [$I > 2\sigma(I)$], 324 parameters, 0 restraints, R1 = 0.060, wR2 (all data) = 0.150.

Crystal data for **7**: $C_{42}H_{44}Zr \cdot 1/2(C_7H_8)$, M_r = 686.06, orange prism, size 0.2 × 0.3 × 0.5 mm, monoclinic, space group $P2_1/c$, a = 17.710(4) Å, b = 10.058(2) Å, c = 19.471(4) Å, β = 93.78(3)°, V = 3460.8(1) Å^3, T = 200 K, Z = 4, ρ_{calcd} = 1.317 g cm^{-3}, μ(Mo Kα) = 3.49 cm^{-1}. F(000) = 1444, 10 074 reflections were measured, 5528 were independent of symmetry, 3945 were

(12) *SHELXS-86*: Sheldrick, G. M. *Acta Crystallogr*. **1990**, *A46*, 467.
(13) Sheldrick, G. M. *SHELXL-93*; University of Göttingen: Göttingen, Germany, 1993.

observed [$I > 2\sigma(I)$], 412 parameters, 0 restraints, R1 = 0.047, wR2 (all data) = 0.125.

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Supporting Information Available: Tables of crystal data, data collection parameters, atomic coordinates, anisotropic displacement parameters, bond distances, and bond angles for complexes **5** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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