Stable *rac*-[1,2-Ethylene-1,1′-bis(η^5-tetrahydroindenyl)]-zirconacyclopentanes. Syntheses, X-ray Crystal Structures, Stability, and Catalysis of Ethylene Polymerization

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The reaction of *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$) (**1**) [ebthi = 1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)] with an excess of ethylene at room temperature leads to the corresponding zirconacyclopentane **3,** which was isolated as stable yellow crystals and characterized by an X-ray crystal structure analysis. At 203 K complex **1** reacts with only 1 equiv of ethylene to form the zirconacyclopentene **2**, possibly an intermediate in the reaction from **1** to **3**. Upon activation with tris(pentafluorophenyl)borane under an ethylene atmosphere, complex **3** was shown to be an effective catalyst for ethylene polymerization. The reaction of 2 equiv of styrene with the alkyne complex **1** leads to the unsymmetrically substituted zirconacyclopentane **6**.

Introduction

Although five-membered zirconacycles often are proved to be intermediates in coupling reactions of unsaturated hydrocarbons with a zirconocene complex fragment,[1a−e] only a few of these metallacycles have been isolated and structurally characterized.[2a−c] In general, the stability decreases from zirconacyclopentadienes to zirconacylopentenes to zirconacyclopentanes. Especially, the zirconacyclopentane system Zr(C_4H_8) was used in metal-assisted coupling reactions[3] and has been investigated spectroscopically.[3,4] Recently a zirconacyclopentane, stabilized by large substituents in the zircona-ring system, was isolated and structurally characterized.[5] Very recently, Takahashi and co-workers reported the isolation and structural characterization of the stable zirconacyclopentane (t-$Bu_2C_5H_3$)$_2$Zr(C_4H_8),[2b] and the structure of the complex $Ind_2Zr(C_4H_8)$[2c] also was briefly mentioned. We report here the preparation and structural characterization of the stable *rac*-[1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)]zirconacyclopentane **3**, starting from the alkyne complex, *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$) (**1**),[6] and the application of complex **3** as an active catalyst for ethylene polymerization upon activation with $B(C_6F_5)_3$. The unusual reaction path from **1** to **3** was investigated by NMR spectroscopy.

Results

The green solution of *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$) (**1**) reacts with an excess of ethylene in toluene at room temperature and changed immediately to yellow, giving after workup under argon yellow crystals of *rac*-(ebthi)-Zr(C_4H_8) (**3**) in 85% yield (Scheme 1).

The crystal structure of **3** is shown in Figure 1. The bond length of C(2)−C(3) [1.451(7) Å] is slightly shorter than that of C(1)−C(2) [1.529(6) Å] and C(3)−C(4) [1.551(7) Å] and coincides with the structures of other unsubstituted zirconacyclopentanes.[2b,c] A conformational disorder which cannot be resolved suggests the shorter $C_\beta-C_{\beta'}$ bond length.

The stepwise formation of **3** was proven by NMR spectroscopy. Special equipment[7] allows NMR spectra to be taken while the gaseous reactant is bubbling into the solution. The progress of the reaction can be monitored by the proton spectra of the cyclopentadienyl ligands, the complexes **1** and **3** showing, due to the C_2 symmetry, two doublets each, whereas the intermediate **2** exhibits four. At room temperature in toluene-d_8 solution, at first only the starting complex **1** is detectable by signals at 7.43 and 4.60 ppm.[6] Upon addition of ethylene, new signals at 6.32 and 4.92 ppm (**3**) appeared, and free bis(trimethylsilyl)acetylene was detected besides several unidentified byproducts. No intermediates could be detected. When we conducted the same experiment at 203 K, complex **1** reacted only with 1 equiv of ethylene to form the zirconacyclopentene **2**, even in the presence of an excess of the olefin. Only the four doublets at 6.66, 6.41, 5.09, and 4.65 ppm, belonging to **2**, were detected. This conversion was quantitative.

At higher temperatures, the zirconacyclopentene **2** is unstable. At about 240 K, its resonances disappeared,

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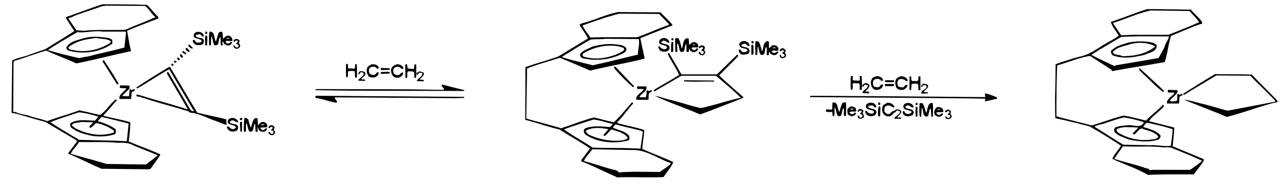
Scheme 1



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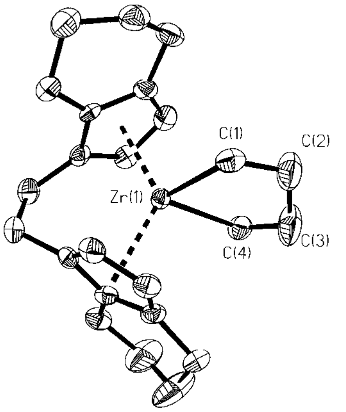

Figure 1. Molecular structure of complex **3**, shown by an ORTEP plot (30% probability). Selected bond distances (Å) and angles (deg): C(1)−Zr, 2.289(4); C(4)−Zr, 2.307(4); C(1)−C(2), 1.529(6); C(2)−C(3), 1.451(7); C(3)−C(4), 1.551(7); C(2)−C(1)−Zr, 101.8(3); C(3)−C(2)−C(1), 113.7(5); C(2)−C(3)−C(4), 116.2(5); C(3)−C(4)−Zr, 100.9(3); C(1)−Zr−C(4), 84.0(2).

several new, unassigned signals grew in, and the signals of the alkyne complex **1** became detectable again, although severely broadened. At the same time, the first traces of the zirconancyclopentane **3** showed up in the spectrum. While the excess of ethylene was removed during the warmup (by bubbling argon into the solution), equal amounts of **1** and **3** were being formed. Formally, a dismutation reaction of the zirconacyclopentene had occurred (Scheme 2).

When ethylene was added again at ambient temperature, the residual alkyne complex **1** was converted into the zirconacyclopentane **3**, whereas all unidentified byproducts remained unchanged.

A very clean reaction was observed in THF-d_8 solution. At 194 K, compound **1** was coordinated by a solvent molecule to give the complex *rac*-(ebthi)Zr(thf)(η^2-$Me_3SiC_2SiMe_3$).[8] Nevertheless, it formed also the zirconacyclopentene **2** in quantitative yield upon exposure to ethylene. At 238 K, the signals of **2** became very broad and a C_1-symmetric, unidentified intermediate was detectible, and at 290 K, conversion to the zirconacyclopentane **3** was complete. No other signals due to ebthi complexes were found in the ^{1}H NMR spectrum.

Another zirconocene−alkyne complex, $Cp_2Zr(thf)(\eta^2$-$Me_3SiC_2SiMe_3)$ (**4**),[9] also reacted with ethylene at room temperature to give the corresponding zirconacyclopentane $Cp_2Zr(C_4H_8)$ (**5**)[2a,3,4] (80% yield, by NMR) (Scheme 3).

The reaction of *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$) (**1**) with substituted ethylenes also was tested. With disubstituted olefins such as 1,1-diphenylethylene and *trans*-stilbene no reaction took place, but with *cis*-stilbene we observed isomerization to *trans*-stilbene as previously described.[10] While the reaction of propene with **1** showed no uniform reaction product, we obtained red crystals of the unsymmetrical substituted zirconacyclopentane *rac*-(ebthi)$\overline{\mathrm{Zr\text{-}CHPhCH_2CHPhCH_2}}$ **6** from the reaction of **1** with two equivalents of styrene in hexane at room temperature (72% yield) according to Scheme 4.

The crystal structure of **6** is shown in Figure 2. The bond length C(2)−C(30) [1.331(6) Å] is significantly shorter than that of C(1)-C(2) [1.481(6) Å] and C(9)−C(30) [1.551(7) Å]. We do not have an explanation for the shorter C_β−$C_{\beta'}$ bond length. Only one of the C_β atoms shows significantly larger displacement factors and thus, conformational disorder as the main reason for significantly shorter C_β−$C_{\beta'}$ distances in comparison to the C_α−$C_{\beta'}$ distances can be excluded. Hence shorter C_β−$C_{\beta'}$ distances seem to be a structural feature of many metallacyclopentanes[2b] including zirconacyclopentanes.[2b,c]

The regioselectivity of the olefin-olefin coupling reactions was found to depend on steric and electronic interactions. Electronically, the α-position is favored,[11] while the repulsion between the tetrahydroindenyl ligand and the phenyl residue should lead to a preferred occupation of the β-position as found in similar Cp*Zr[12] complexes.

Monitoring of the reaction of Scheme 4 by ^{1}H-NMR revealed that a multitude of complexes is formed upon treating the alkyne complex **1** with styrene, probably a mixture of the various possible regio- and stereoisomeric zirconacyclopentanes. Their formation seems to be reversible, and there is strong evidence for an interconversion of the different forms. From this mixture the isomer **6** crystallizes preferentially; presumably it is the least soluble one. If one of the isolated red crystals is dissolved again, several compounds are detectable in the NMR spectrum. This is another indication for the interconversion of the isomers by cycloreversion (*cf.* Scheme 5).

The low selectivity of *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$) (**1**) in coupling reactions with substituted olefins is unexpected because, for example, the heteroolefinic imine PhHC═NPh was coupled very selectively by the (ebthi)Zr unit.[6]

NMR Characterization of the Zirconacyclopentene 2. Since **2** is stable under ethylene at low temperature, it was investigated in detail by NMR methods. At 203 K, the resonances of most aliphatic protons are

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[8] The ^{13}C-NMR signal for the alkyne carbon atoms of complex **1** at 210 K is shifted from 260 ppm in toluene-d_8 to 223 ppm in THF-d_8.

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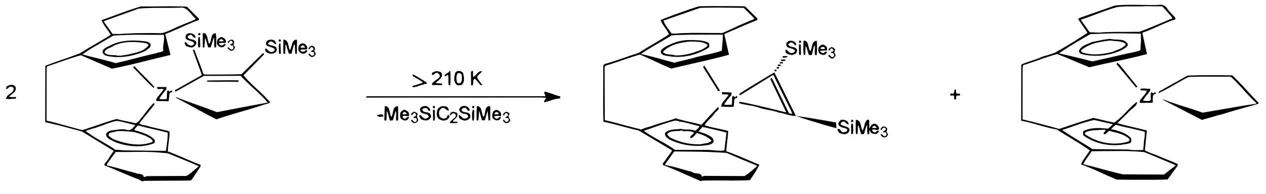
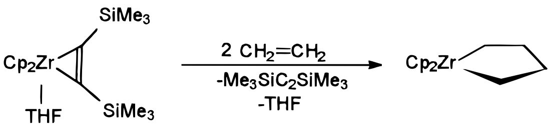
Scheme 2



2 1 3

Scheme 3



4 5

broadened, which might be due to some dynamic processes. A spin saturation transfer experiment with irradiation at the frequency of free ethylene revealed an exchange with four proton sites at the complex (Figure 3), representing the ethylene fragment incorporated in the zirconacycle. The chemical shifts and coupling constants of this system (Figure 3) are typical for saturated hydrocarbons and prove **2** to be a genuine zirconacyclopentene, not a zirconium–alkyne–alkene complex. The existence of a covalent bond between C(2) and C(3) was also deduced from a cross peak in the ^{13}C,^{1}H long-range shift correlation spectrum (COLOC) between the signals of C(1) and the proton site d. The ^{13}C NMR spectrum itself is compatible with the zirconacyclopentene structure. The resonances of the metallacycle were assigned according to known zirconacyclopentenes,[13] although the resonances of **2** are considerably shifted to low field due to the presence of the silyl groups.

As outlined above, the system zirconacyclopentene **2**/ethylene is a dynamic one; there is a rapid exchange between the free ethylene and the ethylene incorporated in the ring. Formally, the C(2)–C(3) bond is broken (a bis-ligand complex is formed (*cf.* Scheme 5)), and the olefin or the alkyne may be easily substituted. This is not unexpected behavior, and it has been observed, particularly for group 4 metallacarbocycles, for some years[14,15] and even was found for a more stable oxazirconacyclopentene.[16] It easily explains not only the dynamic equilibrium between “free” and “complexed” ethylene in **2**, but also the formation of the zirconacyclopentane **3** from the zirconacyclopentene **2** as shown in Schemes 1 and 2.

If the spin saturation transfer experiment as described above is conducted with a solution of the zirconacyclopentane **3** at room temperature, no transfer is observed. The exchange between the “free” and the “complexed” ethylene is very slow, but it should occur, anyway.[14a,15]

Mechanistic Considerations

To our knowledge, this is the first example of the formation of a zirconacyclopentane starting from an alkyne complex. This unusual reaction pathway is due to the special feature of the bis(trimethylsilyl)acetylene ligand, which is reluctant to undergo coupling reactions.[17] This is the reason why the bis(trimethylsilyl)acetylene ligand, in contrast to other alkynes, can even be removed by ethylene.

Takahashi and co-workers investigated in detail the reaction of zirconacyclopentanes with alkynes and observed the totally reverse reaction from zirconacyclopentanes via zirconacyclopentenes to the zirconium alkyne complexes.[3]

In the case of monosilylated alkynes, the low yield of zirconacyclopentenes was explained by a path “where a silylated alkyne kicks out the ethylene molecule of the zirconocene–ethylene complex”. Under ethylene gas they found that this path was completely suppressed and high yields of zirconacyclopentenes were obtained. The reverse reaction, from a zirconacyclopentene to a zirconacyclopentane, never was observed.

Our results suggest that the reaction path and the type of products strongly depend on the alkyne substituents. The reversible formation of the zirconacyclopentene **2** from the alkyne complex **1** and ethylene allows some insight into the mechanism of reactions of bis(trimethylsilyl)acetylene–zirconocene complexes with various substrates.[17] Although we cannot prove that the zirconacyclopentene **2** is the key intermediate in the reaction sequence of Scheme 1, its observation makes it most likely that such reactions proceed in an *associative* (found also in the displacement of other π-compounds[1e]) rather than a *dissociative* manner. The alkyne complexes formally act as metallocene generators, but there is little or no evidence for alkyne dissociation (i) or substitution (ii) to give the metallocene or the substrate complex (Scheme 6).

In contrast, an addition (coupling, insertion) (iii) of the substrate followed by an elimination (iv) or substitution (v) of the alkyne is evident (Scheme 7).

Catalytic Studies. A brief investigation of the catalytic activity of complex **3** also was conducted. Treatment of complex **3** with 1 equiv of tris(pentafluorophenyl)borane under an ethylene atmosphere resulted in the formation of an active ethylene polymerization catalyst. The polymerization productivity was 125 kg of PE per hour, mole zirconium, and bar. The obtained polyethylene products are characterized by $M_w = 49\,900$ and $M_w/M_n = 3.44$. Without an ethylene atmosphere, no activity was achieved by borane activation. Also, a mixture of **1** and tris(pentafluorophenyl)borane did not polymerize ethylene. Interestingly, under analogous conditions, the polymerization of propylene so far was

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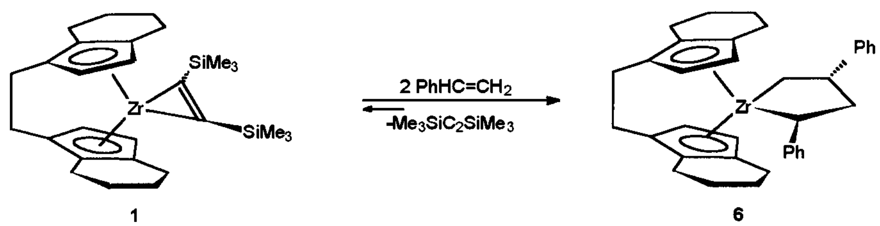
Scheme 4



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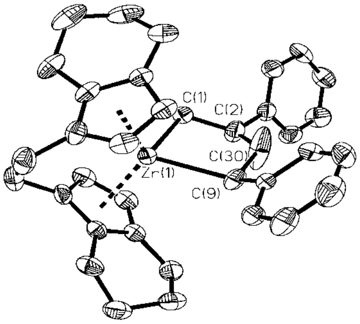


Figure 2. Molecular structure of complex **6**, shown by an ORTEP plot (30% probability). Selected bond distances (Å) and angles (deg): C(1)–Zr, 2.304(4); C(9)–Zr, 2.347(4); C(1)–C(2), 1.481(6); C(2)–C(30), 1.331(6); C(9)–C(30), 1.551(7); C(2)–C(1)–Zr, 102.9(3); C(30)–C(2)–C(1), 115.4(4); C(9)–C(30)–C(2), 124.1(5); C(30)–C(9)–Zr, 99.1(3); C(1)–Zr–C(9), 83.4(2).

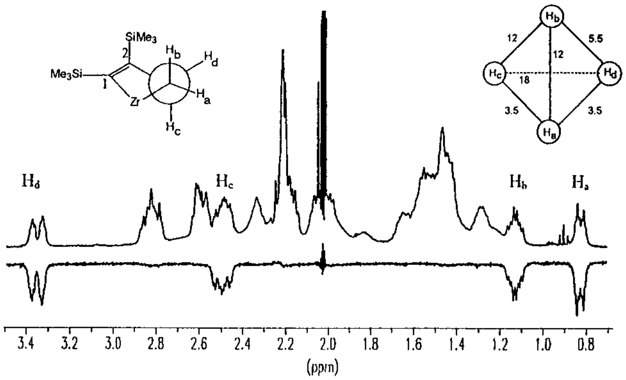
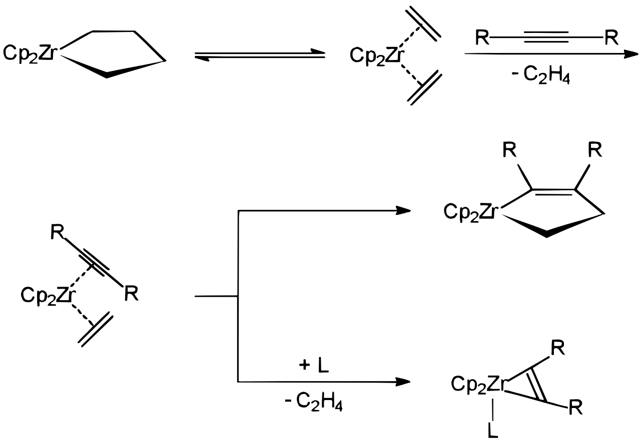


Figure 3. ^{1}H-NMR spectra of the zirconacyclopentene **2** formed under an ethylene atmosphere at 203 K in toluene-d_8. Top trace, standard spectrum; bottom trace, saturation transfer experiment with irradiation at 5.24 ppm (free ethylene), presented as difference spectrum. Coupling constants of the "complexed ethylene" fragment given in hertz.

Scheme 5



not successful. That is in contrast to the well-known activity of other (ebthi)ZrR_2/$B(C_6F_5)_3$ systems.

Experimental Section

All operations were carried out under an inert atmosphere (argon) with standard Schlenk techniques. Prior to use, solvents were freshly distilled from sodium tetraethyl aluminate under argon. Deuterated solvents were treated with sodium or sodium tetraethyl aluminate, distilled, and stored under argon. NMR: Bruker ARX 400 at 9.4 T (chemical shifts given in ppm relative to TMS). Melting points were measured in sealed capillaries on a Büchi 535 apparatus. Elemental analyses: Leco CHNS-932 elemental analyzer.

X-ray Crystallographic Study of Complexes 3 and 6. Diffraction data were collected on a STOE-IPDS diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods (SHELXS-86[18]) and refined by full matrix least squares techniques against F^2 (SHELXL-93[19]). The hydrogen atoms were included at calculated positions. All other nonhydrogen atoms were refined anisotropically. Cell constants and other pertinent data were collected and recorded in Table 1. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. The larger anisotropic displacement factors of the β-C atoms of the zirconacyclopentanes indicate conformational flexibility. Resolution of the different positions was not possible. Further details of the crystal structure investigations are available upon request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ, (U.K.), on quoting the full journal citation.

Observation of *rac*-(ebthi)$\overline{\text{ZrC(SiMe}_3\text{)=C(SiMe}_3\text{)CH}_2\text{CH}_2}$ (2) by NMR Spectroscopy at Low Temperature. Ethylene gas was bubbled slowly into a cooled (200 K) solution of *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$), **1**, in toluene-d_8. The color immediately changed from green to yellow, and complex **2** was formed in quantitative yield, as was checked by NMR at 203 K (see Figure 3). ^{1}H: δ 0.29, 0.30 (9H each, $SiMe_3$), 0.82 (H_a), 1.13(H_b), 2.50 (H_c), 3.36 (H_d), 1.28, 1.47, 1.56, 1.65, 1.83, 2.03, 2.21, 2.34, 2.60, 2.83 (CH_2 ebthi), 4.65, 6.41 (CH ebthi, $^3J_{H,H}$ = 3.1 Hz), 5.09, 6.66 (CH ebthi, $^3J_{H,H}$ = 2.8 Hz). ^{13}C: δ 2.2, 4.9 ($SiMe_3$), 222.8 (C1), 174.3 (C2), 47.7 (C3, $^1J_{C,H}$ = 124 Hz), 31.8 (C4, $^1J_{C,H}$ = 123 Hz), 22.5, 22.7, 22.8, 22.8, 23.1, 23.7, 24.3, 24.5, 25.8, 25.9 (CH_2 ebthi), 104.5, 105.2, 107.9, 116.1 (CH ebthi), 122.0, 122.3, 122.4, 122.6, 125.4, 126.4 (C ebthi).

Preparation of *rac*-(ebthi)$\overline{\text{ZrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$ (3). A solution of 40 mg (76 μmol) of *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$), **1**, in 8 mL of toluene was exposed to an ethylene atmosphere. While the solution was vigorously stirred at room temperature, the color changed from green to yellow within a few minutes. After half of the solvent was removed *in vacuo* and cooled to −40 °C, 26 mg (85%) of bright yellow crystals was obtained, mp 133-136 °C. Anal. Calcd for $C_{24}H_{32}Zr$ (411.74): C, 70.01; H, 7.83. Found: C, 70.02; H, 7.75. ^{1}H-NMR (toluene-d_8): δ 0.39 and 1.34 (1-H, 4-H), 1.83 and 1.95 (2-H, 3-H), 1.68, 2.18,

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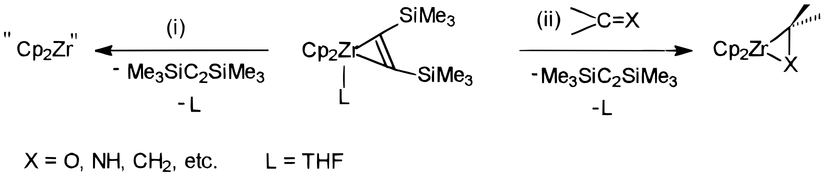
Scheme 6



Scheme 7

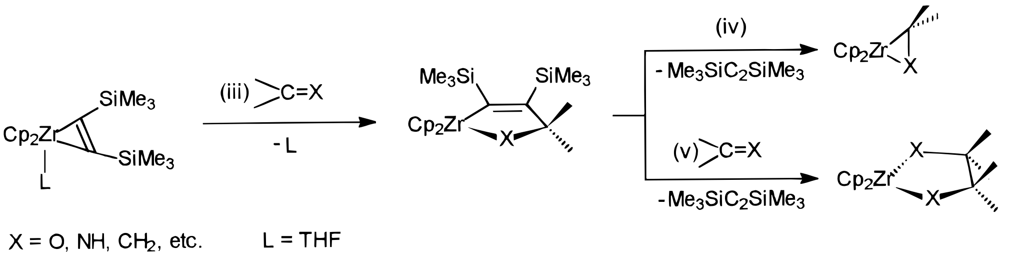


Table 1. Crystallographic Data of 3 and 6

	3	6
formula	$C_{24}H_{32}Zr$	$C_{36}H_{40}Zr$
mol mass	411.72	563.90
cryst color, habit	yellow, prismatic	red, prismatic
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
lattice constants		
a (Å)	9.941(2)	11.000(2)
b (Å)	11.702(3)	11.607(2)
c (Å)	16.571(3)	21.789(2)
β (deg)	94.930(10)	94.780(15)
Z	4	4
temp (K)	200(2)	293(2)
μ(Mo Kα) (cm^{-1})	5.7	4.2
θ range (deg)	2.13−24.24	1.88−24.35
no. of rflns (measd)	8068	8075
no. of rflns (indep)	3037	4258
no. of rflns (obsd)	2084	2779
no. of parameters	226	334
RI ($I > 2\sigma(I)$)	0.040	0.044
wR2 (all data)	0.094	0.108

2.72, 3.04 (α-H six-membered rings), 1.34, 1.51, 1.56 (β-H six-membered rings), 2.31 (c, AA′BB′ pattern, ethylene bridge ebthi), 4.92, 6.32 (CH ebthi, $^3J_{H,H} = 3$ Hz). ^{13}C-NMR (toluene-d_8): δ 45.4 (C1, C4), 28.1 (C2, C3), 23.3, 23.4, 24.0, 24.8, 28.1 (CH_2 ebthi), 108.1, 112.4 (CH ebthi), 123.5, 124.9, 125.7 (C ebthi).

Preparation of $Cp_2ZrCH_2CH_2CH_2CH_2$ (5). A solution of 25 mg (52 μmol) of $Cp_2Zr(thf)(\eta^2\text{-}Me_3SiC_2SiMe_3)$, **4**, in 0.4 mL of THF-d_8 was exposed to an ethylene atmosphere. After 1 min the color of the solution changed from red to yellow and the product was detected by NMR. **5** is stable at room temperature in THF. ^{1}H-NMR: δ 0.91 (1-H, 4-H), 1.70 (2-H, 3-H), 6.28 (Cp). ^{13}C-NMR: δ 40.4 (C1, C4), 29.7 (C2, C3), 111.9 (Cp).

Preparation of *rac*-(ebthi)ZrCHPhCH$_2$CHPhCH$_2$ (6). To a solution of 81 mg (154 μmol) of *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$), **1**, in 10 mL of hexane was added 35.2 μL (308 μmol) of styrene. The reaction mixture was warmed to 50 °C for 10 min and the color changed from green to red. After the mixture was left to stand at room temperature, 62 mg (72%) of red crystals was obtained, mp 185−187 °C. Anal. Calcd for $C_{36}H_{40}Zr$ (563.93): C, 76.67; H, 7.15. Found: C, 76.61; H, 7.20.

Polymerization of Ethylene. Polymerization was conducted in a 50 mL Schlenk tube, using a solution of 5 mg (12 μmol) of complex **3** and 6 mg (12 μmol) of tris(pentafluorophenyl)borane in 2 mL of toluene at room temperature under a constant ethylene pressure of 2 bar. The mixture was stirred vigorously, and after a reaction time of 10 min, the reaction mixture was drained from the Schlenk tube into a mixture of 40 mL of ethanol and 1 mL of concentrated aqueous HCl. The polymer thus precipitated was collected by filtration and dried at room temperature to constant weight (0.5 g yield).

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Supporting Information Available: Tables of crystal structure parameters and details of data collection, bond angles and distances, atomic positional and thermal parameters, and ORTEP diagrams **3** and **6** (10 pages). Ordering information is given on any current masthead page.

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