Reactive Intermediates of the Catalytic Carbomagnesation Reaction: Isolation and Structures of $[Cp_2ZrEt]_2(\mu$-ethene), $[Cp_2Zr(ethene)(L)]$ (L = THF, Pyridine), and $[(indenyl)_2Zr(ethene)(THF)]$ and of Metallacycles with Norbornene†

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The reaction between Cp_2ZrCl_2 and 2 equiv of EtMgCl in THF at 0 °C results in the formation of the binuclear complex $[Cp_2Zr(Et)]_2(\mu$-ethene) (**1**) in good yield. An X-ray crystallographic structure determination of **1** shows that the bridging ethene can be considered as the dianion $C_2H_4^{2-}$ which is asymmetrically coordinated to the two neighboring $Cp_2Zr(Et)$ centers. The analogous complex $[(Me_3Si\text{-}Cp)_2Zr(Et)]_2(\mu$-ethene) (**2**) was isolated from the reaction of $(Me_3Si\text{-}Cp)_2ZrCl_2$ and 2 equiv of EtMgCl. The mononuclear orange compound $[Cp_2Zr(ethene)(THF)]$ (**3**) was obtained by reaction of Cp_2ZrCl_2 and Et_2Mg(dioxane) in THF below 0 °C. In the ^{1}H NMR spectrum of **3** in THF-d_8 at 0 °C only two singlets were observed (5.46 and 0.51 ppm, respectively), corresponding to the Cp and the ethene protons. Furthermore, its structural motif in the solid state was determined by X-ray crystallography at −90 °C. The closely related complexes $[(indenyl)_2Zr(ethene)(THF)]$ (**4**) and $[Cp_2Zr(ethene)$-(pyridine)] (**5**) were analogously prepared in good yield. The X-ray structure of the dark red complex **4** shows that the zirconium atom, the two carbons of ethene, and the oxygen donor atom of THF lie in a single plane. The C−C bond distance of the coordinated ethene is elongated to 1.451(5) Å. Complex **3** undergoes a fast reaction with norbornene to form the metallacycle **6**, which was characterized by NMR spectroscopy in solution and by X-ray diffraction analysis in the solid state as well. The complexes **1**, **3**, and **6** are isolated compounds which are involved in the Cp_2ZrX_2-catalyzed carbomagnesation reaction of norbornene with EtMgX.

Introduction

Since the first work by Dzhemilev[1] on catalytic carbomagnesation of olefins, this has become an established method for synthesizing special Grignard reagents useful for preparing functionalized organic molecules.[2−17] In the 1990s Hoveyda and co-workers developed the highly regio- and stereoselective synthesis of functionally substituted compounds using catalytic carbomagnesation.[5−11] The reactivity of in situ generated Cp_2ZrEt_2 to form ethene complexes as well as zirconacycles was investigated by Negishi,[12] leading to a plausible mechanism of the carbomagnesation process (Scheme 1). Other investigations by Hoveyda,[5] Waymouth,[13] and Whitby[14] supported this mechanism. In the catalytic cycle the ethene complex **A** (Scheme 1), formed by β-hydride elimination from Cp_2ZrEt_2, may play an essential role as a likely intermediate. It is also proposed that subsequent reaction of **A** with an olefin results in the metallacycle **B**, which subsequently further undergoes transmetalation with EtMgX to form

† This work is dedicated to Prof. Karl Heinz Thiele (Halle, Germany) on the occasion of his 70th birthday.

(1) (a) Dzhemilev, U. M.; Vostrikova, O. S.; Sultanov, R. M. *Izv. Akad. Nauk SSSR, Ser. Khim* **1983**, *32*, 213. (b) Dzhemilev, U. M.; Vostrikova, O. S.; Sultanov, R. M.; Kukovinets, A. G.; Khalikov, A. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1983**, *32*, 2035.
(2) Dzhemilev, U. M.; Vostrikova, O. S. *J. Organomet. Chem.* **1985**, *285*, 43.
(3) Dzhemilev, U. M.; Ibragimov, A. G.; Zolotarev, A. P.; Mulukhov, R. R.; Tolstikov, G. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1989**, *38*, 207.
(4) Dzhemilev, U. M.; Sultanov, R. M.; Gaimaldinov, R. G.; Tolstikov, G. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1991**, *40*, 1388.
(5) Hoveyda, A. H.; Xu, Z. *J. Am. Chem. Soc.* **1991**, *113*, 5079.
(6) Hoveyda, A. H.; Xu, Z.; Morken, J. P.; Houri, A. F. *J. Am. Chem. Soc.* **1991**, *113*, 8950.
(7) Hoveyda, A. H.; Morken, J. P.; Houri, A. F.; Xu, Z. *J. Am. Chem. Soc.* **1992**, *114*, 6692.
(8) Houri, A. F.; Didiuk, M. T.; Xu, Z.; Horan, N. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1993**, *115*, 6614.
(9) Hoveyda, A. H.; Morken, J. P. *J. Org. Chem.* **1993**, *58*, 4237.
(10) Morken, J. P.; Didiuk, M. T.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1993**, *115*, 6997.
(11) Morken, J. P.; Didiuk, M. T.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1994**, *116*, 3123.
(12) (a) Takahashi, T.; Seki, T.; Nitto, Y.; Saburi, M.; Rousset, C. J.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 6266. (b) Takahashi, T.; Suzuki, N.; Kageyama, M.; Nitto, Y.; Saburi, M.; Negishi, E. *Chem. Lett.* **1991**, 1579. (c) For a recent review see: Negishi, E.; Takahashi, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 755 and references therein.
(13) Knight, K. S.; Waymouth, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 6268.
(14) Lewis, D. P.; Muller, P. M.; Whitby, R. J.; Jones, R. V. H. *Tetrahedron Lett.* **1991**, *32*, 6797.
(15) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047.
(16) Negishi, E.; Kondakov, D. Y. J. *Chem. Soc. Rev.* **1996**, 4117 and references therein.
(17) Negishi, E. Takahashi, T. *Acc. Chem. Res.* **1994**, *27*, 124.

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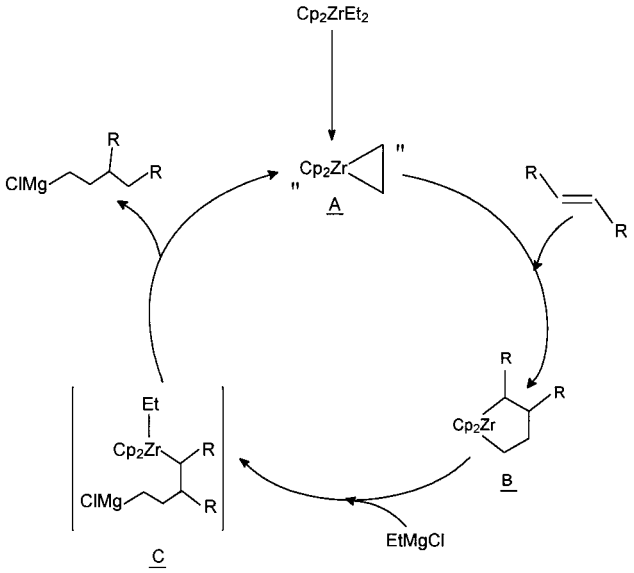
Scheme 1. Proposed Catalytic Cycle of the Carbomagnesation Reaction[5,12,−14]



the Et−Zr species **C**. Subsequent β-hydride elimination followed by elimination of the organomagnesium product **D** and formation of "Cp_2Zr(ethene)" (**A**) are considered to be the last steps, thus closing the catalytic cycle (Scheme 1).

More detailed investigations of the regio- and stereoselectivities of the catalytic carbomagnesation reaction showed, however, that the mechanism might be more complicated, involving more catalytically active species. For example, Hoveyda proposed a catalytic cycle which includes a bis(zirconocene) complex as an intermediate for the formation of the zirconacyclopentane **B**.[8] Moreover, the ethene-containing species **A** was proposed to react with an excess of EtMgBr to give the intermediate $[Cp_2Zr(Et)(ethene)]^-MgBr^+$.[7]

Interestingly, so far neither **A** nor any other intermediate of the catalytic cycle have been isolated and structurally characterized under conditions which facilitate the carbomagnesation reaction. However, some complexes of the type Cp_2Zr(olefin)(PMe_3) were prepared and structurally characterized.[23−28] Furthermore, the X-ray structures of a number of metallacycles formed from α,ω-olefins or 2 equiv of monoolefins are known.[32] In this connection, the question arises whether it is possible to gain a deeper insight into this catalytic reaction through the isolation of intermediates of the catalytic cycle under typical carbomagnesation reaction conditions.

In this paper we report three isolated intermediates of the catalytic carbomagnesation and related complexes. The binuclear ethene ethyl complex **1** was characterized by NMR spectroscopy and by X-ray crystallography. **1** may act as a reservoir for the formation of catalytically active species **A**, which was suggested to be "Cp_2Zr(ethene)" (Scheme 1[5,7,13−17]). Despite the fact that this compound is extremely reactive, we were able to isolate this key complex, which has the composition [Cp_2Zr(ethene)(THF)] (**3**). In addition, we could isolate and structurally characterize two closely related mononuclear ethene complexes (complexes **4** and **5**, respectively). Additionally, we synthesized and characterized the metallacycles **6** and **7** (**B** in Scheme 1) under conditions of the catalytic carbomagnesation reaction using norbornene as substrate.

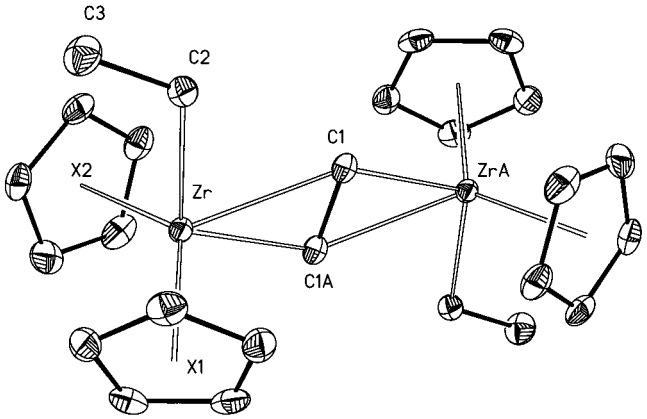


Figure 1. Molecular structure of complex **1.** Selected bond distances (Å) and bond angles (deg): Zr−C1 = 2.534(3), Zr−C1A = 2.335(3), Zr−C2 = 2.365(3), Zr−X1 = 2.240(3), Zr−X2 = 2.243(3) (X1, X2 = centroids of Cp), Zr−X3 = 2.319(3) (X3 = centroid of C1−C1A), C1−C1A = 1.497(5), C2−C3 = 1.533(4); X1−Zr−X2 = 129.7(1), X1−Zr−X3 = 110.5(1), X1−Zr−C2 = 102.6(1), X2−Zr−X3 = 110.0(1), X2−Zr−C2 = 101.7(1), X3−Zr−C2 = 95.9(1), Zr−C1−ZrA = 144.5(1), Zr−C2−C3 = 119.9(2). Symmetry transformation used to generate equivalent atoms: (A) $-x, -y, -z + 1$.

Results

The Complexes [$Cp_2Zr(Et)]_2$(μ-ethene) (1) and [(Me_3Si-Cp)$_2$Zr(Et)]$_2$(μ-ethene) (2): On the Way to the Catalytically Active Species. Treatment of Cp_2ZrCl_2 in concentrated THF solution with 2 equiv of EtMgCl at 0 °C resulted in the liberation of ethane and an orange solution within a few minutes. After a short time complex **1** crystallized in yellow prisms together with magnesium salts. To remove small amounts of $MgCl_2(THF)_n$, the isolated product was recrystallized from THF, yielding yellow crystals suitable for an X-ray crystal structure determination. Under conditions of the catalytic carbomagnesation reaction (excess of EtMgCl, presence of norbornene as possible substrate) **1** can be obtained as well, provided the reaction is carried out with high concentrations of the reaction partners at 0 °C.

Figure 1 displays the molecular structure of **1** and contains relevant bond lengths and angles. Complex **1** is binuclear, with the composition $Cp_2Zr(Et)(\mu$-ethene)-$Zr(Et)Cp_2$, which has an inversion center. The metals and the carbon atoms C(1), C(2), and C(3) lie in a plane. Furthermore, the C=C bond length (1.497(5) Å) in the C_2H_4 bridge is remarkably elongated compared with the length in the free olefin. In addition, the ethene ligand adopts the trans bent distorted coordination geometry with two distinctly different Zr−C bond distances of 2.365(3) and 2.534(3) Å, respectively. From these data we conclude that the C_2H_4 ligand can be considered as a C_2H_4 dianion, comparable with its coordination in similar complexes (vide infra).

According to the ^{1}H NMR spectra in THF-d_8, the resonances of the ethene protons give rise to a singlet at high field (−0.46 ppm). The signal for the CH_2 protons

of the ethyl group is found at 0.59 ppm and that for the CH_3 group at 1.30 ppm, whereas the resonance of the Cp protons appears as a singlet at 5.66 ppm. As expected for this binuclear structure, only four signals are observed the ^{13}C NMR spectrum measured in THF-d_8 solution. The resonance for the CH_2 carbons of the olefin occurs at 11.9 ppm and the Cp carbon resonances appear at 106.8 ppm. Furthermore, two signals due to the carbon atoms of the ethyl group are observed at 18.3 and 24.3 ppm.

These data suggest that the binuclear structure of **1** is maintained in solution as well. Moreover, NOE NMR measurements reveal that the hydrogen atoms of the ethylene bridge are in close proximity of the CH_2 group of each ethyl ligand. In the solid state as well, the distance H(1)···H(2) and the distance H(1a)···H(2a) are relatively short (2.481(5) and 2.377(5) Å, respectively).

Compound **1** is sparingly soluble in THF and in aromatic solvents and is stable in the solid state at ambient temperature.

For further comparison, we have reacted $(Me_3Si\text{-}Cp)_2ZrCl_2$ with 2 equiv of EtMgCl as well and isolated the related binuclear complex $[(Me_3Si\text{-}Cp)_2Zr(Et)]_2(\mu\text{-ethene})$ (**2**). Complex **2** is more soluble than **1** and is even more stable toward β-hydride elimination than compound **1**. Its NMR spectra are similar to those of complex **1**. The protons of the bridging ethene appear at −0.27 ppm, and the ethyl protons display resonances at 0.90 and 1.66 ppm, respectively. As expected, there are four signals for the Me_3Si-Cp ligand between 5.59 and 6.08 ppm. Additionally, the protons of the Me_3Si substituent are found at 0.29 ppm.

Several binuclear Zr complexes containing ethene as a bridge between two Zr centers have been reported. One of the first examples, $[Cp_2Zr(Cl)AlEt_2]_2(\mu\text{-ethene})$, was structurally characterized by Kaminsky and Sinn.[18] Cotton investigated the halogeno complexes $[X_3Zr(PEt_3)_2]_2(\mu\text{-ethene})$ (X = Cl, Br),[19] and the methyl compound $[Cp_2Zr(Me)]_2(\mu\text{-ethene})$ was prepared and structurally elucidated by Takahashi and Negishi.[20] Recently Royo and Berke investigated the complex $[L_2ZrEt]_2(\mu\text{-ethene})$ (L_2 = bis(dimethylsilanediyl)dicyclopentadienyl) and determined its structure by X-ray diffraction analysis. Additionally, characteristic data of this compound were calculated by DFT.[21] A comparison of the structural and NMR data of these binuclear compounds with those of complex **1** indicates that the coordination geometry and the bond distances of the ethene ligand in **1** are essentially identical.

We assume that **1** is the first stable product in the formation process of the catalytically active ethene zirconium complex. Despite the fact that **1** contains two β-hydrogen containing ethyl groups, it is thermally stable at room temperature in the solid state. Moreover, the compound can be recrystallized from warm THF. The Me_3Si-substituted derivative **2** is even more stable toward β-hydride elimination.

Mononuclear Olefin Complexes $[Cp_2Zr(ethene)(THF)]$ (3), $[(indenyl)_2Zr(ethene)(THF)]$ (4), and $[Cp_2Zr(ethene)(pyridine)]$ (5): Complex 3 as Reactive Intermediate of the Catalytic Carbomagnesation. To isolate the mononuclear ethene complex "Cp_2Zr(ethene)", which was proposed as the key species in the catalytic carbomagnesation reaction, we have carried out a variety of reactions. Despite the fact that a number of other Cp_2Zr olefin complexes were studied in solution,[7,15−17,22,25] to the best of our knowledge, to date only mononuclear Cp_2Zr(olefin) complexes were isolated which are stabilized by phosphines. For example, $Cp_2Zr(ethene)(PMe_3)$ was prepared and structurally characterized by Alt[23] and by Binger.[24] Complexes with other olefins containing PMe_3 as additional ligand also have been isolated.[25−28]

Remarkably, when we reacted a EtMgCl/norbornene/Cp_2ZrCl_2/PMe_3 mixture (molar ratio 5:2:1:1) in THF at room temperature, no carbomagnesation reaction occurred, whereas the same mixture reacted smoothly to form the carbomagnesation product in high yields when PMe_3 was absent. In other words, occupation of one coordination position of the Zr center by PMe_3 inhibits the catalysis.

When we carried out the reaction of a concentrated THF solution of Cp_2ZrCl_2 with EtMgCl at −20 °C, large amounts of $MgCl_2(THF)_n$ precipitated, together with a very small amount of an orange compound which could not be separated from the pasty reaction mixture. This substance proved to be very reactive and decomposed above 0 °C. Since this compound could be the active zirconocene ethene intermediate in the catalytic carbomagnesation cycle, we varied the reaction conditions and succeeded in the isolation of this orange complex by reacting pure Et_2Mg(dioxane) with Cp_2ZrCl_2. Under these conditions only half of the amount of magnesium salts obtained above is formed.

Et_2Mg(dioxane) was readily prepared from EtMgCl in diethyl ether.[29] After addition of dioxane the white precipitate was separated at room temperature. Colorless crystals of Et_2Mg(dioxane) (**8**) suitable for an X-ray crystal structure determination were isolated from the filtrate at −20 °C in good yields.

Figure 2 displays its molecular structure and lists selected bond lengths and angles. As expected, the Mg center is tetrahedrally coordinated and surrounded by two carbon atoms of the ethyl groups and two oxygen atoms of the dioxane molecule, which acts as a bridging ligand, yielding a polymeric chain.

(18) Kaminsky, W.; Kopf, J.; Sinn, H.; Vollmer, H.-J. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 629.
(19) Cotton, F. A.; Kibala, P. A. *Inorg. Chem.* **1990**, *29*, 3192.
(20) Takahashi, T.; Kasai, K.; Suzuki, N.; Nakajima, K.; Negishi, E. *Organometallics* **1994**, *13*, 3413.
(21) Fernandez, F. J.; Gomez-Sal, P.; Manzanero, A.; Royo, P.; Jacobsen, H.; Berke, H. *Organometallics* **1997**, 1553.
(22) (a) Van Wangen, B. C.; Livinghouse, T. *Tetrahedron Lett.* **1989**, *30*, 3495. (b) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1987**, *27*, 2829.
(23) Alt, H. G.; Denner, C. E.; Thewalt, U.; Rausch, M. *J. Organomet. Chem.* **1988**, *356*, C83.
(24) Binger, P.; Müller, P.; Benn, R.; Rufinska, A.; Gabor, B.; Krüger, C. *Chem. Ber.* **1989**, *122*, 1035.
(25) (a) Takahashi, T.; Tamura, M.; Saburi, M.; Uchida, Y.; Negishi, E. *J. Chem. Soc., Chem. Commun.* **1989**, 852. (b) Takahashi, T.; Musukami, M.; Saburi, M.; Kozawa, K.; Uhida, Y.; Swansson, D. R.; Negishi, E. *Chem. Lett.* **1989**, 761.
(26) Takahashi, T.; Nitto, Y.; Seki, T. Saburi, M.; Negishi, E. *Chem. Lett.* **1990**, 2259 and references therein.
(27) Swanson, D. R.; Negishi, E. *Organometallics* **1991**, *10*, 825.
(28) (a) Fisher, R. A.; Buchwald, S. L. *Organometallics* **1990**, *9*, 871. (b) Buchwald, R. L.; Kreutzer, K. A.; Fisher, R. *J. Am. Chem. Soc.* **1990**, *112*, 4600.
(29) (a) Schlenk, W.; Schlenk, W. *Chem. Ber.* **1929**, *62*, 920. (b) Schlenk, W. *Chem. Ber.* **1931**, *64*, 734.

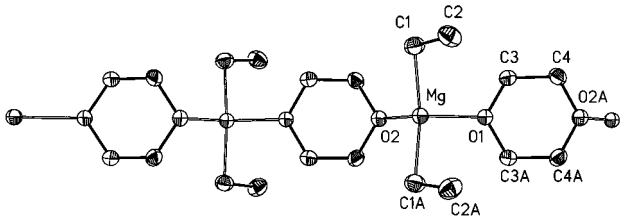


Figure 2. Molecular structure of complex **8**. Selected bond distances (Å) and bond angles (deg): Mg−C1 = 2.142(2), Mg−O1 = 2.077(2), Mg−O2 = 2.084(2), C1−C2 = 1.531(2), O1−C3 = 1.441(2), C3−C4 = 1.489(2), C4−O2A = 1.445(2); O1−Mg−O2 = 100.29(7), O1−Mg−C1 = 104.16(5), O2−Mg−C1 = 107.21(5), C1−Mg−C1A = 129.9(1), Mg−C1−C2 = 111.2(1). Symmetry transformation used to generate equivalent atoms: (A) $x, -y + {}^1/_2, z$.

The reaction to isolate the extremely reactive orange ethene complex **3** was carried out as follows: treatment of **8** with 1 equiv of Cp_2ZrCl_2 in THF/HMDS (hexamethyldisiloxane) (1:1 mixture) at −78 °C and warming to −20 °C resulted in the evolution of ethane and formation of an orange solution. The reaction was allowed to proceed at 0 °C, and then the mixture was cooled to −20 °C. The magnesium salts which precipitated were filtered. At −20 °C orange needles of complex **3** crystallized.

3 is extremely sensitive toward air and moisture. Furthermore, it decomposes above 0 °C. In noncoordinating solvents, in a fast reaction, it gives unidentified products. However, it can be handled at 0 °C for a short time. This allowed the recording of its ^{1}H NMR spectrum in THF-d_8. In a very simple pattern, besides the resonances of the solvent protons, only two singlets were observed at 0 °C. The Cp protons give a singlet at 5.46 ppm, which is only slightly shifted compared with that of **1**. Another remarkable feature of **3** is the significant downfield shift of the singlet due to the ethene protons to 0.51 ppm. These signals are very similar to those detected in a solution of Cp_2ZrCl_2 and 2 equiv of EtMgBr in THF-d_8 (assigned to in situ formed "Cp_2Zr(ethylene)").[12b]

The ratio between the Cp and the C_2H_4 protons in **3** is 10:4, indicating that one ethene ligand is coordinated at the Cp_2Zr moiety, yielding a mononuclear complex. As exposed, the ^{13}C NMR spectrum of **1** at 0 °C exhibits a resonance at 33.5 ppm for coordinated ethene and a resonance for the Cp ring carbon atoms at 104.7 ppm.

The singlet due to the C_2H_4 protons in **3**, as observed at 0 °C, splits into two triplets at 0.26 and 0.95 ppm when the spectrum was recorded at −78 °C in THF-d_8. These results may indicate that the exchange reaction of coordinated THF with the solvent THF is too slow on the NMR time scale to be observed at −78 °C, in contrast to the exchange at 0 °C.

As expected, the ^{13}C NMR spectrum at −78 °C also showed two resonances (at 27.7 and 36.8 ppm) for the C_2H_4 carbon atoms. Temperature-dependent spectra to determine the free energy of activation of the THF exchange are also discussed in connection with ligand exchange reactions of the similar complexes **4** and **5** (vide infra).

A low-temperature X-ray determination of **3** was carried out. However, due to the poor quality of the crystals only the structural motif could be determined, showing, without doubt, the mononuclear complex [Cp_2Zr(ethene)(THF)], in which one ethene molecule as well as a THF molecule is coordinated to Zr (Figure 3).

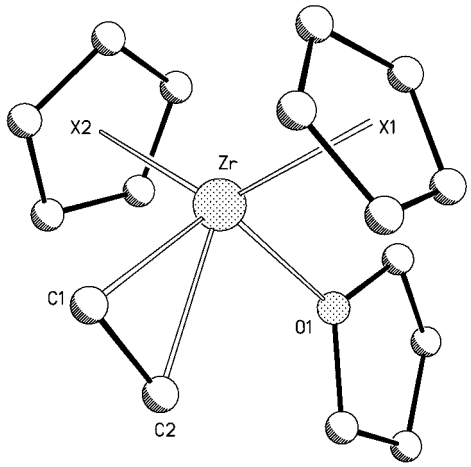


Figure 3. Structural motif of complex **3**.

^{1}H NMR measurements at 0 °C in THF-d_8 clearly showed that complex **3** immediately reacts with norbornene to give the metallacycle **6**, which was characterized by NMR spectroscopy and in the solid state by X-ray crystallography (Figure 6, vide infra).

Furthermore, **3** reacts with 1 equiv of Et_2Mg(dioxane) (**8**) in THF-d_8 to give a yellow solution. According to the ^{1}H NMR spectrum at 0 °C, the product formed in this reaction contains two different ethyl groups (CH_3 at 1.17 ppm and CH_2 at −0.76 ppm, J = 8.2 Hz; CH_3 at 1.30 ppm and CH_2 at 0.31 ppm, J = 7.5 Hz), and one ethene molecule per Cp_2Zr unit. The protons of the coordinated ethene appear as two triplets at −1.75 and 0.52 ppm, respectively. Comparing these data with those of the binuclear compound **1** and of Et_2Mg(dioxane) (**8**), we assume that the reaction product could be binuclear, analogously to **1**, containing, however, one $MgEt(THF)_n$ moiety in place of the Cp_2Zr(Et) fragment. The ^{13}C NMR data agree with this assumption as well (see Experimental Section).

The corresponding indenyl complex **4** was isolated by reacting (indenyl)$_2ZrCl_2$ with Et_2Mg(dioxane) in THF/HMDS following the procedure described for the analogous cyclopentadienyl complex **3**. The compound [(indenyl)$_2$Zr(ethene)(THF)] (**4**) forms dark red crystals and crystallizes with 0.5 $MgCl_2(THF)_4$ per zirconium, suitable for a low-temperature X-ray structure determination. The high quality of the data set allowed solution and refinement of all hydrogen atom positions in this complex. Figure 4 shows the molecular structure and lists relevant bond distances and angles.

The mononuclear complex is best described as a distorted tetrahedron with the Zr in the center, in which the indenyl ligands are considered to occupy one coordination position each. The other two positions are occupied by the THF oxygen donor atom and the midpoint of the coordinated ethene. Additionally, the zirconium, the ethene carbon atoms, and the oxygen atom of THF lie in a single plane with the metal center. The Cp(centroid)−Zr−Cp(centroid) angle is 136.0(1)°. The Zr−C bonds to the coordinated ethene lie within the normal range (2.334(3) and 2.292(3) Å, respectively). The C−C bond of the coordinated ethene is elongated to 1.451(5) Å, indicating that complex **4** may be described as zirconacyclopropane containing Zr(IV) rather

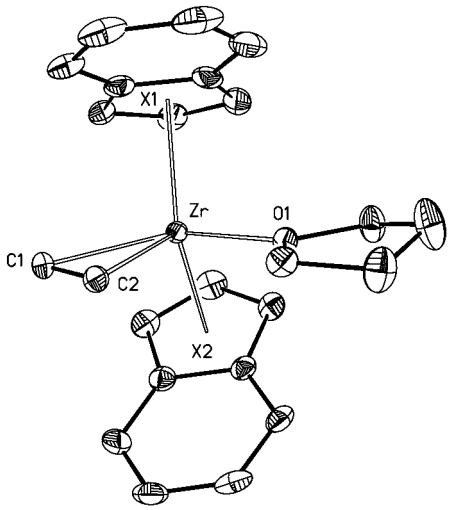


Figure 4. Molecular structure of complex **4**. $MgCl_2(THF)_4$ is omitted for clarity. It shows no interaction with the organometallic molecule. Selected bond distances (Å) and bond angles (deg): Zr−C1 = 2.334(3), Zr−C2 = 2.292(3), Zr−O1 = 2.363(2), Zr−X1 = 2.269(3), Zr−X2 = 2.264(3) (X1, X2 = centroids of Cp), Zr−X3 = 2.196(3) (X3 = centroid of C1−C2), C1−C2 = 1.451(5); X1−Zr−X2 = 136.0(1), X1−Zr−X3 = 107.6(1), X1−Zr−O1 = 100.5(1), X2−Zr−X3 = 105.8(1), X2−Zr−O1 = 101.3(1), X3−Zr−O1 = 99.6(1).

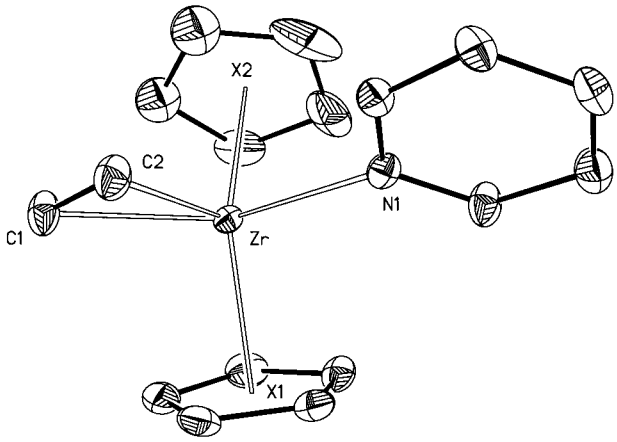


Figure 5. Molecular structures of complex **5**. Selected bond distances (Å) and bond angles (deg): Zr−C1 = 2.341(6), Zr−C2 = 2.304(8), Zr−N1 = 2.487(6), Zr−X1 = 2.243(8), Zr−X2 = 2.242(8) (X1, X2 = centroids of Cp), Zr−X3 = 2.206(8) (X3 = centroid of C1−C2), C1−C2 = 1.455-(9); X1−Zr−X2 = 133.2(2), X1−Zr−X3 = 110.2(2), X1−Zr−N1 = 101.8(2), X2−Zr−X3 = 107.4(2), X2−Zr−N1 = 98.3(2), X3−Zr−N1 = 99.9(2).

than an ethene−Zr(II) complex. The Zr−O(1) distance of 2.363(2) Å is relatively long, suggesting a weak bond.[30]

Additionally, we have prepared [Cp_2Zr(ethene)(pyridine)] (complex **5**), which can be synthesized analogously to the THF-containing complex **3** by reacting Cp_2ZrCl_2 and Et_2Mg(dioxane) in a mixture of diethyl ether/HMDS and pyridine at −20 °C. Complex **5** was obtained as a dark brown crystalline solid which is extremely air-, temperature-, and water-sensitive. Single crystals of **5** were obtained at −20 °C. Its molecular structure was confirmed by low-temperature X-ray crystallography. Compound **5** crystallized in two independent molecules in the unit cell. Both molecules exhibit similar bond distances and angles. One of the molecules is shown in Figure 5, whose caption shows selected bond lengths and angles.

The molecular structure of **5** is quite similar to that of complex **4**. The pyridine ligand occupies one position in the plane formed by the Zr center and the two carbon atoms of the ethene ligand. The Zr−N distances are quite long (2.477(6) and 2.4688(11) Å, respectively) and lie in the upper region of Zr−N bond lengths.[31] The C═C bond distances are comparable with those in complex **4** (1.455(10) and 1.470(19) Å, respectively).

The NMR spectra of **4** and **5** are nearly similar to those of **3**. For example, the ethene complex **4** shows two proton resonances at −70 °C and two ^{13}C resonances of the C_2H_4 ligand as well, while only one resonance was found at 0 °C (see Experimental Section).

Table 1. Free Activation Energy $\Delta G^{\ddagger}$ for the Exchange of the Ligand (THF or Pyridine) with the Solvent

complex	T_c (K)	$\Delta\nu$ (Hz)	$\Delta G^{\ddagger}$ (kJ mol^{-1})
[Cp_2Zr(ethene)(THF)] (**3**)	220.5	93.1	43.6 ± 0.5
[(indenyl)$_2$Zr(ethene)(THF)] (**4**)	253	630	46.3 ± 0.5
[Cp_2Zr(ethene)(pyridine)] (**5**)	293	133.3	57.7 ± 0.5

The free energies of activation for the THF or pyridine exchange reaction for the complexes **3**−**5**, determinated from the coalescence temperatures and the signal separation of the proton resonances, are listed in Table 1. The THF-containing complexes **3** and **4** have lower $\Delta G^{\ddagger}$values than the corresponding complex **5**, which contains the more strongly coordinated pyridine. Furthermore, [Cp_2Zr(ethene)(THF)] (complex **3**) is more reactive toward THF exchange than [(indenyl)$_2$Zr-(ethene)(THF)] (complex **4**).

In contrast, complexes containing PMe_3 as stabilizing ligand did not show any ligand exchange, even at room temperature.[23] This is in agreement with the fact that PMe_3 complexes are thermally more stable and are inactive in the catalytic carbomagnesation reaction.

Zirconacycles 6 and 7. When [Cp_2Zr(ethene)(THF)] (**3**) (generated either in situ or as the isolated complex) in diethyl ether/THF was reacted with 1 equiv of norbornene at 0 °C, a coupling reaction occurred, resulting in zirconacycle **6** in good yield. Upon filtration of the magnesium salts, complex **6** crystallized at −78 °C to form orange-red crystals suitable for an X-ray structural analysis. The molecular structure is shown in Figure 6. In complex **6** ethene and norbornene are *endo* linked to form a racemate. In the crystals both optical isomers are present in a 1:1 ratio. Remarkably, the C−C bond distance in the norbornane fragment is unusually long (1.593(4) Å). Other relevant bond distances and angles are collected in Figure 6.

A number of X-ray structural analyses of other zirconacyclopentanes have been described. However, these compounds have been prepared either from in situ

(30) (a) Eberle, M.; Rohr, C. *Acta Crystallogr., Sect. C* **1996**, *52*, 566. (b) Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486. (c) Schweder, B.; Görls, H.; Walther, D. *Inorg. Chim. Acta* **1999**, *286*, 14. (d) Rosenthal, U.; Ohff, A.; Michalik, M.; Görls, H.; Burlakov, V. V.; Shur, V. B. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1193.

(31) (a) Troyanov, S. I. *Koord. Khim.* **1987**, *13*, 1123. (b) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 894. (c) Kempe, R.; Spannenberg, A.; Lefeber, C.; Zippel, T.; Rosenthal, U. *Z. Kristallogr.−New Cryst. Struct.* **1998**, *213*, 791. (d) Rosenthal, U.; Ohff, A.; Baumann, W.; Tillack, A.; Görls, H.; Burlakov, V. V.; Shur, V. B. *Z. Anorg. Allg. Chem.* **1995**, *621*, 77.

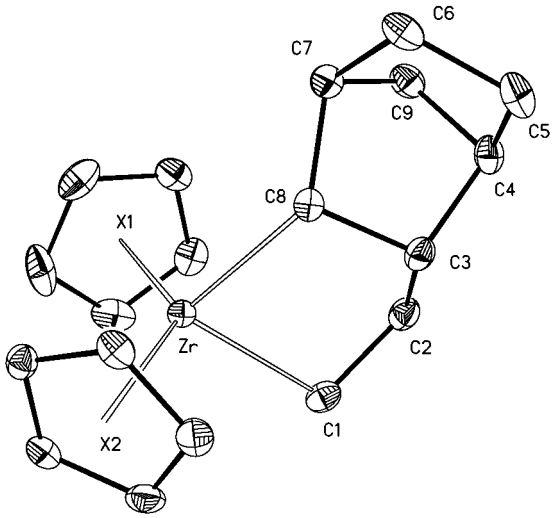


Figure 6. Molecular structure of complex **6**. Selected bond distances (Å) and bond angles (deg): Zr−C1 = 2.294(3), Zr−C8 = 2.313(3), Zr−X1 = 2.241(3), Zr−X2 = 2.242(3) (X1, X2 = centroids of Cp), C1−C2 = 1.545(4), C2−C3 = 1.549(4), C3−C4 = 1.543(4), C3−C8 = 1.593(4); X1−Zr−X2 = 132.5(1), X1−Zr−C1 = 106.3(1), X1−Zr−C8 = 110.9(1), X2−Zr−C1 = 106.3(1), X2−Zr−C8 = 106.5(1), C1−Zr−C8 = 83.0(1).

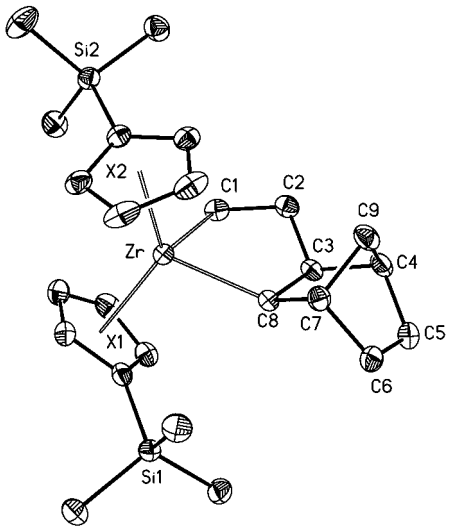


Figure 7. Molecular structure of complex **7**. Selected bond distances (Å) and bond angles (deg): Zr−C1 = 2.303(2), Zr−C8 = 2.325(2), Zr−X1 = 2.258(2), Zr−X2 = 2.240(2) (X1, X2 = centroids of Cp), C1−C2 = 1.536(4), C2−C3 = 1.548(4), C3−C4 = 1.541(3), C3−C8 = 1.597(3); X1−Zr−X2 = 130.6(1), X1−Zr−C1 = 106.7(1), X1−Zr−C8 = 108.1(1), X2−Zr−C1 = 108.2(1), X2−Zr−C8 = 110.0(1), C1−Zr−C8 = 83.0(1).

formed "Cp_2Zr^{II}" (Negishi's reagent) and α,ω-diolefins or by coupling of 2 equiv of a monoolefin.[32]

The ^{1}H NMR spectrum of **6** displays the expected pattern characteristic for the presence of the pure compound in solution. The resonances of both Cp rings are different and give two signals. As expected, the ^{13}C NMR spectrum displays 11 distinct ^{13}C resonances.

Additionally, the reaction between $(Me_3Si\text{-}Cp)_2ZrCl_2$, EtMgCl, and norbornene in diethyl ether/THF resulted in the formation of the corresponding zirconacycle **7**. The NMR data and X-ray crystallographic results for **6** and **7** are comparable (Figure 7).

Discussion

The isolation of **1**, **3**, and **6** and of closely related complexes provides additional insight into the course of the catalytic carbomagnesation reaction. The pathways illustrated in Scheme 2 provide a plausible explanation for the fact that reactions between Cp_2ZrCl_2 and EtMgCl or Et_2Mg(dioxane) give either **1** or **3**, depending on the reaction conditions. In the first step, Cp_2ZrEt_2, formed by reaction of the starting reactants, undergoes elimination of ethane to form the mononuclear ethene complex **3**. The latter may react with excess Cp_2ZrEt_2 to form the binuclear compound **1**. Since this reaction, carried out at 0 °C in concentrated THF, is faster than the possible coupling with norbornene to form the metallacycle **6**, the presence of norbornene does not prevent the formation of **1**, which crystallizes from solution.

When the same reaction was carried out between −20 and 0 °C, a slow heterogeneous reaction occurred between Cp_2ZrCl_2 and the organomagnesium compound to yield Cp_2ZrEt_2, followed by a fast β-hydride elimination and subsequent elimination of ethane to give **3**. However, because under these conditions there is only a small amount of Cp_2ZrEt_2 in solution and the rate of the bimolecular reaction to give **1** is slower, complex **3** reacts only sparingly with Cp_2ZrEt_2 to yield the compound **1**. This might be the explanation why the extremely reactive mononuclear intermediate **3** can be isolated. In the presence of norbornene, however, the C,C-coupling reaction proceeds more rapidly to form **6**.

Monitoring the catalytic carbomagnesation reaction by ^{1}H NMR spectroscopy clearly shows that only the organometallics **1** and **6** are present, while **3** is not observed. This is in agreement with the high reactivity displayed by **3**. Furthermore, after a number of catalytic cycles the binuclear compound **1** is still present in solution. This leads to the conclusion that **1** might act as a reservoir for the formation of **3** during the catalysis. Additionally, **1** might also be formed in a side reaction of the catalytic cycle, in which the metallacycle **6** reacts with 2 equiv of EtMgX, resulting in the formation of the 1.4-dimagnesium reagent[14] and Cp_2ZrEt_2. The latter may react to form the compound **1** according to the above-described transformations (Scheme 2).

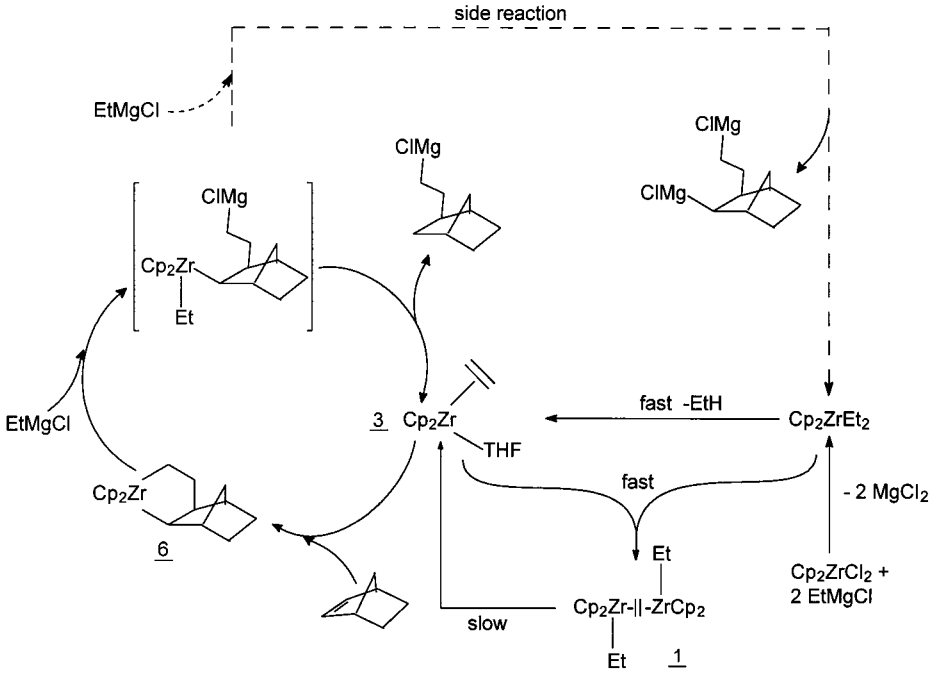
Conclusion

In conclusion, we have isolated and characterized three zirconocene complexes (**1**, **3**, and **6**) which are involved in the catalytic carbomagnesation cycle. While the binuclear compound **1** and the metallacycle **6** could be shown to take part in the catalytic cycle by ^{1}H NMR spectroscopy, the mononuclear compound **3** ([Cp_2Zr(ethene)(THF)]) is too reactive to be observed by ^{1}H NMR during the course of the catalytic reaction.

The only difference between the species **A**, proposed as the key intermediate of the catalytic carbomagnesa-

(32) (a) Taber, D. F.; Louey J. P.; Wang, Y.; Nugent, W. A.; Dixon, D. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1994**, *116*, 9457. (b) Knight, K. S.; Wang, D.; Waymouth, R. M.; Ziller, J. *J. Am. Chem. Soc.* **1994**, *116*, 1845. (c) Takahashi, T.; Fischer, R.; Zhengfeng, X.; Nakajima, K. *Chem. Lett.* **1996**, 357. (d) Mansel, S.; Thomas, D.; Lefeber, C.; Heller, D.; Kempe, R.; Baumann, W.; Rosenthal, U. *Organometallics* **1997**, *16*, 2886.

Scheme 2. Catalytic Cycle of the Carbomagnesation Reaction, Including the Results of This Work



tion, and complex **3** is the coordination of a solvent molecule at the metal center in complex **3**. Since the catalytic carbomagnesation usually proceeds in THF (or in diethyl ether), we can conclude that **A** and **3** are identical species. Additionally, we obtained and characterized the closely related mononuclear zirconium ethene complexes **4** and **5**.

Experimental Section

General Procedures. All reactions and analytical investigations were conducted under an atmosphere of dry argon using standard Schlenk techniques. Prior to use, tetrahydofuran, diethyl ether, dioxane, and HMDS were dried over potassium hydroxide and distilled from sodium benzophenone ketyl. Cp_2ZrCl_2, and Grignard reagents (Aldrich) were used as received; norbornene and (trimethylsilyl)cyclopentadiene were distilled prior to use using standard methods.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 F spectrometer. Elemental analyses were performed with Leco CHNS-932.

Since the complexes **3**, **4**, and **5** decomposed at 0 °C, elemental analyses could not be carried out.

$(Cp_2ZrEt)_2(\mu$-ethene) (1). To a stirred solution of Cp_2ZrCl_2 (2.92 g, 10.0 mmol) in THF (20 mL) at 0 °C was added 19 mL of EtMgBr (1.1 M in THF) via syringe. The reaction mixture turned from colorless to yellow and later to orange. Fine yellow crystals of **1** precipitated a few minutes later. The solid was isolated by filtration, washed twice with THF, and dried in vacuo (0.78 g, 29% yield). Single crystals of **1** suitable for X-ray analysis were obtained from a saturated THF solution at 40 °C. Anal. Calcd for $C_{26}H_{34}Zr_2$: C, 59.03; H, 6.48. Found: C, 58.59; H, 6.53. ^{1}H NMR (200 MHz, THF-d_8): δ −0.46 (4H, s, $=CH_2Zr$), 0.59 (4H, q, J = 7.6 Hz, CH_2Zr), 1.30 (6H, t, J = 7.6 Hz, CH_3), 5.66 (20H, s, Cp). ^{13}C NMR (50.3 MHz, THF-d_8): δ 11.9 ($=CH_2Zr$), 18.3 (CH_3), 24.3 (CH_2Zr), 106.8 (Cp).

$[(Me_3Si\text{-}Cp)_2Zr(Et)]_2(\mu$-ethene) (2). Compound **2** (172 mg, 21% yield) was obtained as a yellow crystalline solid from the reaction of $(Me_3Si\text{-}Cp)_2ZrCl_2$ (875 mg, 2.0 mmol) and Et_2Mg(dioxane) (357 mg, 2.1 mmol) in ether (5 mL) at 0 °C for 15 min. Anal. Calcd for $C_{38}H_{66}Si_4Zr_2$: C, 55.81; H, 8.13. Found: C, 55.38; H, 7.82. ^{1}H NMR (200 MHz, C_6D_6): δ −0.27 (4H, s, $=CH_2Zr$), 0.29 (36H, s, $SiMe_3$), 0.90 (4H, q, J = 7.5 Hz, CH_2-Zr), 1.66 (6H, t, J = 7.5 Hz, CH_2), 5.59 (4H, m, CH), 5.66 (4H, m, CH), 6.01 (4H, m, CH), 6.08 (4H, m, CH). ^{13}C NMR (50.3 MHz, C_6D_6): δ 0.7 ($SiMe_3$), 12.0 ($=CH_2Zr$), 20.6 (CH_3), 24.3 (CH_2Zr), 108.2 (CH), 110.6 (C−Si), 111.9 (CH), 114.3 (CH), 118.1 (CH).

$[Cp_2Zr(ethene)(THF)]$ (3). Et_2Mg(dioxane) (0.357 g, 2.1 mmol) was dissolved in a mixture of HMDS (6 mL) and THF (6 mL). After it was cooled to −78 °C, Cp_2ZrCl_2 (0.584 g, 2.0 mmol) was added to the stirred solution. The slurry was warmed to −20 °C, resulting in a yellow solution which slowly turned to orange. The stirred solution was kept for 1 min in an ice bath. Then it was cooled again to −20 °C. The precipitate of magnesium chloride was separated at this temperature. The filtrate was stored at −20 °C. Red-orange needles of **3** crystallized from the solution. They are very sensitive to air and moisture. **3** is only stable at temperatures below 0 °C. ^{1}H NMR (200 MHz, THF-d_8, 0 °C): δ 0.51 (4H, s, CH_2), 5.46 (10H, s, Cp). ^{1}H NMR (THF-d_8, −80 °C): 0.26 (2H, t, J = 10.3 Hz, CH_2), 0.95 (2H, t, J = 10.3 Hz, CH_2), 5.46 (10H, s, Cp). The temperature of coalescence is T_c = 220.5 K. ^{13}C NMR (50.3 MHz, THF-d_8, 0 °C): δ 26.3 (CH_2, ^1J(CH) = 131.8 Hz), 33.5 ($=CH_2$, ^1J(CH) = 143.5 Hz); 68.3 (O-CH_2, ^1J(CH) = 144.5 Hz), 104.7 (Cp, ^1J(CH) = 169.8 Hz, ^{3}J(CH) = 6.8 Hz). ^{13}C NMR (THF-d_8, −80 °C): δ 27.7 ($=CH_2$), 36.8 ($=CH_2$), 104.7 (Cp).

$[(indenyl)_2Zr(ethene)(THF)]\cdot 0.5MgCl_2(THF)_4$ (4). The dark red compound **4** was prepared from $(indenyl)_2ZrCl_2$ (0.784 g, 2.1 mmol) and Et_2Mg(dioxane) (0.357 g, 2.1 mmol) in a solution of THF (6 mL) and HMDS (6 mL) via the procedure outlined for **3**. ^{1}H NMR (200 MHz, THF-d_8, 0 °C): δ −1.43 (4H, br, $=CH_2$), 5.70 (6H, s, CH), 6.78 (4H, m, CH), 7.07 (4H, m, CH). ^{1}H NMR (THF-d_8, −70 °C): δ −2.29 (2H, t, J = 11.1 Hz, CH_2), 0.86 (2H, t, J = 11.1 Hz, CH_2), 5.68 (2H, br, 2-CH), 5.76 (4H, br, 1-CH, 3-CH), 6.78 (4H, m CH), 7.07 (4H, m, CH). The temperature of coalescence is T_c = 253 K. ^{13}C NMR (50.5 MHz, THF-d_8, −70 °C): δ 49.4 ($=CH_2$, ^1J(CH) = 145.1 Hz), 52.1 ($=CH_2$, ^1J(CH) = 144.8 Hz), 81.6 (CH), 89.7 (CH), 107.3 (CH), 122.7 (CH), 123.1 (CH), 123.3 (CH), 123.7 (CH), 126.3 (C).

$[(Cp_2Zr(ethene)(pyridine)]$ (5). Dark brown crystals of **5** were obtained by reaction of Et_2Mg(dioxane) (0.357 g, 2.1 mmol) with Cp_2ZrCl_2 (0.584 g, 2.1 mmol) in a solution of pyridine (2 mL), ether (5 mL), and HMDS (2 mL) by following the same procedure as described for **3**. ^{1}H NMR (200 MHz, pyridine-d_5, −10 °C): δ 0.69 (2H, t, J = 10.5 Hz, $=CH_2$), 1.35

(2H, t, J = 10.5 Hz, =CH_2), 5.55 (10H, s, Cp). The temperature of coalescence is T_c = 293 K. ^{13}C NMR (50.3 MHz, pyridine-d_5, −10 °C): δ 27.8 (=CH_2, ^1J(CH) = 140.0 Hz), 35.4 (=CH_2, ^1J(CH) = 142.8 Hz), 104.2 (^1J(CH) = 170.1 Hz, ^3J(CH) = 6.8 Hz).

$Cp_2Zr(C_2H_4$-$C_7H_{10})$ (6). To a stirred suspension of Cp_2ZrCl_2 (2.92 g, 10.0 mmol) in diethyl ether (60 mL) at −78 °C were added 5 mL of Et_2Mg(dioxane) (2 M in diethyl ether) and norbornene (0.9 g, 9 mmol). The reaction mixture was warmed to 0 °C. After the mixture was stirred for 12 h at this temperature, the precipitate of magnesium chloride was separated. **6** crystallized as red crystals from the filtrate at −78 °C. Yield: 1.35 g (42%). Anal. Calcd for $C_{19}H_{24}Zr$: C, 66.41; H, 7.04. Found: C, 66.43; H, 7.28. ^{1}H NMR (200 MHz, C_6D_6): δ 5.86 (5H, s, Cp), 5.82 (5H, s, Cp), 0.48 (1H, t, CH_2-Zr), 0.45 (1H, t, CH_2-Zr). ^{13}C NMR (50.3 MHz, C_6D_6): δ 111.6 (Cp), 110.8 (Cp), 63.0 (CH-Zr), 50.6 (CH), 45.6 (CH), 44.6 (CH), 39.6 (CH_2-Zr), 36.9 (CH_2), 36.8 (CH_2), 29.5 (CH_2), 27.3 (CH_2).

$(Me_3Si$-$Cp)_2Zr(C_2H_4$-$C_7H_{10})\cdot 0.5$(dioxane) (7). Preparation of **7**, yielding red crystals, was carried out by a procedure similar to that described for **6**, starting from $(Me_3SiCp)_2ZrCl_2$ (53% yield). Anal. Calcd for $C_{27}H_{44}OSi_2Zr$: C, 60.95; H, 8.34. Found: C, 61.02; H, 8.08. ^{1}H NMR (C_6D_6): δ 6.83 (1H, m, CH), 6.63 (1H, m, CH), 6.59 (2H, m, CH), 5.89 (1H, m, CH), 5.82 (3H, m, CH), 3.53 (4H, s, CH_2O), 0.07 (9H, s, Me_3Si), 0.14 (9H, s, Me_3Si). ^{13}C NMR (50.3 MHz, C_6D_6): δ 122.7 (C−Si), 121.7 (CH), 120.4 (CH), 118.7 (CH), 117.9 (CH), 115.0 (CH), 113.4 (CH), 120.8 (CH), 67.7 (CH_2O), 62.3 (CH-Zr), 55.1 (CH), 45.5 (CH), 45.3 (CH), 41.1 (CH_2-Zr), 36.7 (CH_2), 36.5 (CH_2), 29.6 (CH_2), 28.9 (CH_2), 0.0 (Me_3Si).

Et_2Mg(dioxane)[29] (8). A solution of EtMgBr (100 mL, 10 mmol) in diethyl ether was slowly treated with dioxane (14 mL, 0,16 mmol). The white precipitate was separated by filtration and washed with diethyl ether. At −20 °C white crystals of **8** were isolated from the filtrate. Yield: 11.1 g (65%). ^{1}H NMR (200 MHz, THF-d_8): δ −0.83 (4H, q, J = 8.2 Hz, CH_2-Mg), 1.14 (6H, t, J = 8.2 Hz, CH_3), 3.53 (8H, s, CH_2O). ^{13}C NMR (50.3 MHz, THF-d_8): δ −2.3 (CH_2Mg), 14.2 (CH_3), 67.7 (CH_2O).

Reaction of $[Cp_2Zr$(ethene)(THF)] (3) with Et_2Mg-(dioxane) (8). To Cp_2ZrCl_2 (146 mg, 0.5 mmol) dissolved in THF-d_8 (1.0 mL) was added solid **8** (170 mg, 1.0 mmol) at −40 °C. The reaction mixture was warmed to 0 °C. During this period the color of the reaction mixture turned from colorless to yellow. ^{1}H NMR (in situ) (200 MHz, THF-d_8, 0 °C): δ −1.75 (2H, t, J = 9.6 Hz, =CH_2), − 0.76 (2H, q, J = 8.2 Hz, CH_2Mg), 0.31 (2H, q, J = 7.5 Hz, CH_2Zr), 0.52 (2H, t, J = 9.6 Hz, =CH_2), 1.17 (3H, t, J = 8.2 Hz, CH_3), 1.30 (3H, t, J = 7.5 Hz, CH_3), 3.53 (8H, s, CH_2O), 5.19 (10 H, s, Cp). ^{13}C NMR (in situ) (200 MHz, THF-d_8, 0 °C): δ −20.5 (Mg-CH_2=), −2.2 (Mg-CH_2−), 14.4 (CH_3), 16.9 (Zr-CH_2−), 18.6 (CH_3), 31.0 (Zr-CH_2=), 103.1 (Cp).

X-ray Crystallography. The intensity data for the compound **8** were collected on a Nonius CAD4 diffractometer and for the other compounds on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects, but not for absorption.[33,34]

The structures were solved by direct methods (SHELXS[35]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[36]). For the compounds **1**, **6**, **7**, and **8** and for the ethene group of **4** the hydrogen atoms were located by difference Fourier syntheses and refined isotropically; the hydrogen atoms of the other structures were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[36] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. Since we could not obtain crystals of sufficient quality for compound **3,** we have only published the crystallographic data and the conformation of the molecule. We will not deposit the data of **3** in the Cambridge Crystallographic Data Centre. For the compounds **1**, **6**, **7**, and **8** and for the ethylene group of **4** the hydrogen atoms were located by difference Fourier syntheses and refined isotropically; the hydrogen atoms of the other structures were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[36] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal data for **1**:[37] $C_{26}H_{34}Zr_2$, M_r = 528.97, yellow prism, size 0.30 × 0.30 × 0.04 mm^3, orthorhombic, space group *Pbca*, a = 13.1399(3) Å, b = 8.1659(3) Å, c = 21.0520(8) Å, α = 90.00°, β = 90.00°, γ = 90.00°, V = 2258.86(13) Å^3, T = −90 °C, Z = 4, ρ_{calcd} = 1.555 g cm^{-3}, μ(Mo Kα) = 9.31 cm^{-1}, F(000) = 1080, 13 477 reflections in h (−15 to +16), k (−10 to +8), l (−26 to +25), measured in the range 3.09° ≤ θ ≤ 26.38°, completeness θ_{max} = 99.8%, 2315 independent reflections, R_{int} = 0.057, 1906 reflections with $F_o > 4\sigma(F_o)$, 196 parameters, 0 restraints, $R1_{obsd}$ = 0.030, $wR2_{obsd}$ = 0.067, $R1_{all}$ = 0.044, $wR2_{all}$ = 0.072, GOF = 1.065, largest difference peak/hole 0.617/−0.766 e Å^{-3}.

Crystal data for **3**: $C_{12}H_{14}O_2Zr$, M_r = 281.45, red prism, size 0.32 × 0.22 × 0.12 mm^3, triclinic, space group $P\bar{1}$, a = 7.2728-(15) Å, b = 7.6173(15) Å, c = 7.6573(15) Å, α = 90.83(3)°, β = 112.87(3)°, γ = 109.04(3)°, V = 364.58(13) Å^3, T = −90 °C, Z = 1, ρ_{calcd} = 1.282 g cm^{-3}, μ(Mo Kα) = 7.36 cm^{-1}, F(000) = 142, 2571 reflections in h (−9 to +9), k (−9 to +9), l (−9 to +9), measured in the range 3.35° ≤ θ ≤ 27.57°, completeness θ_{max} = 97.6%.

Crystal data for **4**:[37] $C_{24}H_{26}OZr\cdot{}^1/_2MgCl_2O_4C_{16}H_{32}$, M_r = 613.48, brown prism, size 0.32 × 0.28 × 0.22 mm^3, triclinic, space group $P\bar{1}$, a = 8.0453(3) Å, b = 9.2152(3) Å, c = 21.3220-(7) Å, α = 85.627(2)°, β = 84.132(2)°, γ = 71.987(2)°, V = 1493.77(9) Å^3, T = −90 °C, Z = 2, ρ_{calcd} = 1.364 g cm^{-3}, μ(Mo Kα) = 4.98 cm^{-1}, F(000) = 642, 9768 reflections in h (−10 to +10), k (−11 to +11), l (−27 to +24), measured in the range 4.09° ≤ θ ≤ 27.47°, completeness θ_{max} = 96.1%, 6568 independent reflections, R_{int} = 0.027, 5656 reflections with $F_o > 4\sigma(F_o)$, 337 parameters, 0 restraints, $R1_{obsd}$ = 0.052, $wR2_{obsd}$ = 0.118, $R1_{all}$ = 0.064, $wR2_{all}$ = 0.124, GOF = 1.037, largest difference peak/hole 0.764/−0.741 e Å^{-3}.

Crystal Ddata for **5**:[37] $C_{17}H_{19}N$ Zr, M_r = 328.55, brown prism, size 0.32 × 0.22 × 0.12 mm^3, orthorhombic, space group $P2_12_12_1$, a = 7.8643(2) Å, b = 15.7119(7) Å, c = 24.053(1) Å, V = 2972.1(2) Å^3, T = −90 °C, Z = 8, ρ_{calcd} = 1.469 g cm^{-3}, μ(Mo Kα) = 7.26 cm^{-1}, F(000) = 1344, 6516 reflections in h (−9 to +9), k (−20 to +20), l (−31 to +31), measured in the range 3.09° ≤ θ ≤ 27.49°, completeness θ_{max} = 97.5%, 6516 independent reflections, 4949 reflections with $F_o > 4\sigma(F_o)$, 289 parameters, 0 restraints, $R1_{obsd}$ = 0.060, $wR2_{obsd}$ = 0.125, $R1_{all}$ = 0.088, $wR2_{all}$ = 0.137, GOF = 1.039, Flack parameter 0.37(9), merohedral twin refinement, largest difference peak/hole 0.970/−0.876 e Å^{-3}.

Crystal data for **6**:[37] $C_{19}H_{24}Zr$, M_r = 343.60, orange prism, size 0.32 × 0.20 × 0.10 mm^3, monoclinic, space group $P2_1/n$, a = 9.7897(8) Å, b = 12.753(1) Å, c = 12.332(1) Å, β = 91.567-(5)°, V = 1539.1(2) Å^3, T = −90 °C, Z = 4, ρ_{calcd} = 1.483 g cm^{-3},

(33) MOLEN, An Interactive Structure Solution Procedure; Enraf-Nonius, Delft, The Netherlands, 1990.
(34) Otwinowski, Z.; Minor, W. Processing of X-ray Diffraction Data Collected in Oscillation Mode. In *Methods in Enzymology*; Carter, C. W., Sweet, R. M., Eds.; Academic Press: New York, 1997; Vol. 276 (Macromolecular Crystallography, Part A), pp 307−326.
(35) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.
(36) Sheldrick, G. M. SHELXL-97; University of Göttingen, Göttingen, Germany, 1993.
(37) Further details of the crystal structure investigations are available on requests from the director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1 EZ, U.K., on quoting the depository numbers CCSD-139465 (**1**), CCSD-139467 (**4**), CCSD-139466 (**5**), CCSD-139468 (**6**), CCSD-139469 (**7**), and CCSD-139470 (**8**), the names of the authors, and the journal citation.

μ(Mo Kα) = 7.03 cm^{-1}, F(000) = 712, 6201 reflections in h (−12 to +12), k (−16 to +16), l (−1 to +15), measured in the range 3.07° ≤ θ ≤ 27.50°, completeness θ_{max} = 99.4%, 3509 independent reflections, R_{int} = 0.031, 2866 reflections with $F_o > 4\sigma(F_o)$, 278 parameters, 0 restraints, $R1_{obsd}$ = 0.039, $wR2_{obsd}$ = 0.082, $R1_{all}$ = 0.055, $wR2_{all}$ = 0.088, GOF = 1.033, largest difference peak/hole 0.480/−0.803 e Å^{-3}.

Crystal data for **7**:[37] $C_{27}H_{44}OSi_2Zr$, M_r = 532.02, orange prism, size 0.32 × 0.28 × 0.20 mm^3, triclinic, space group $P\bar{1}$, a = 9.7465(5) Å, b = 10.5015(5) Å, c = 14.9963(7) Å, α = 106.162(3)°, β = 98.653(2)°, γ = 104.702(2)°, V = 1385.0(1) Å^3, T = −90 °C, Z = 2, ρ_{calcd} = 1.276 g cm^{-3}, μ(Mo Kα) = 5.0 cm^{-1}, F(000) = 564, 11 486 reflections in h (−12 to +12), k (−13 to +13), l (−19 to +19), measured in the range 3.31° ≤ θ ≤ 27.51°, completeness θ_{max} = 99.2%, 6319 independent reflections, R_{int} = 0.028, 5471 reflections with $F_o > 4\sigma(F_o)$, 456 parameters, 0 restraints, $R1_{obsd}$ = 0.041, $wR2_{obsd}$ = 0.085, $R1_{all}$ = 0.055, $wR2_{all}$ = 0.090, GOF = 1.078, largest difference peak/hole 0.297/−0.450 e Å^{-3}.

Crystal data for **8**:[37] $C_8H_{18}MgO_2$, M_r = 170.53, colorless prism, size 0.40 × 0.40 × 0.32 mm^3, orthorhombic, space group $Pnma$, a = 11.731(3) Å, b = 13.661(4) Å, c = 6.555(1) Å, V = 1050.5(4) Å^3, T = −90 °C, Z = 4, ρ_{calcd} = 1.078 g cm^{-3}, μ(Mo Kα) = 1.27 cm^{-1}, F(000) = 376, 1898 reflections in h (0 to +17), k (0 to +20), l (0 to +9), measured in the range 2.98° ≤ θ ≤ 32.03°, 1898 independent reflections, 1154 reflections with $F_o > 4\sigma(F_o)$, 91 parameters, 0 restraints, $R1_{obsd}$ = 0.043, $wR2_{obsd}$ = 0.1083, $R1_{all}$ = 0.098, $wR2_{all}$ = 0.132, GOF = 1.039, largest difference peak/hole 0.183/−0.233 e Å^{-3}.

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Supporting Information Available: X-ray structural information on the complexes **1**, **4**, **5**, **6**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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