(μ-Methylene)bis(methylzirconocene): Preparation, Molecular Structure, and Thermal Disproportionation

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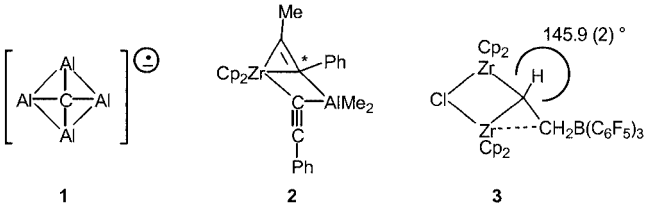
The title compound $[(\mu\text{-}CH_2)(ZrCp_2Me)_2]$ (**4**) was prepared by the reaction of $[Cp_2Zr(Cl)Me]$ (**6**) with $CH_2(MgBr)_2$ (**5**) or $(CH_2Mg)_n$ (**7**). It had been expected that the carbon atom bridging the two zirconium atoms of **4** might be a candidate for a planar tetracoordinate carbon atom, but the X-ray crystal structures of two different modifications (crystals 1 and 2) showed it to be non-planar; however, the widened Zr–C–Zr angle of 132.7(1) and 134.0(3)°, respectively, and an unsymmetrical coordination of the central μ-CH_2 group (average: Zr1–CH_2 2.225 Å, Zr2–CH_2 2.242 Å) indicates a tendency towards planarity. While **4** is relatively stable in THF solution, it disproportionates in toluene solution to give the 1,3-dizirconacyclobutane $(Cp_2ZrCH_2)_2$ (**8**) and $[Cp_2ZrMe_2]$ (**9**), especially in the presence of magnesium salts; a tentative mechanism is presented. Reaction of **4** with $B(C_6F_5)_3$ yielded the methyl-bridged cationic complex **17**, which, on treatment with trityl chloride, was transformed into the corresponding chloro complex **18**; the latter was characterized by an X-ray crystal structure determination. With THF and tetrahydrothiophene, **17** formed the unsymmetrical adducts **19a** and **19b**, respectively; NMR spectroscopic data revealed dynamic symmetrization due to methyl-group exchange at 280 and 213 K, respectively.

Introduction

Tetracoordinate carbon centers strongly prefer a tetrahedral geometry, as is common knowledge since the early work of van't Hoff and Le Bel.[1] Two strategies have been applied to stabilize the unfavorable planar geometry: one of them uses strain to force the carbon atom into planarity, the other stabilizes the planar carbon atom electronically by di- or polysubstitution with metal atoms.[2−5]

Thus, in the gas phase, the Al_4C^- ion (**1**; Scheme 1) has been shown by PES spectroscopy and by calculation to have a planar D_{4h} symmetry.[4] Erker et al. have been successful in preparing stable compounds involving a planar tetracoordinate carbon atom incorporated into a π- or an aromatic system such as **2**; the asterisk marks the planar carbon atom.[6] Another example of such a dimetallic compound is **3**. In this case the planarity around the carbon atom was not effected, but a widening of the Zr−CH−CH_2 angle approaching local C_{2v} symmetry, as indicated in Scheme 1, shows the incipient tendency of this carbon atom to become severely distorted as well.[7]



1 2 3

Scheme 1

It remains a challenge to try and prepare a stable planar tetracoordinate saturated carbon atom. In this context, we investigated the possibility that the methylene carbon atom in $[(\mu\text{-}CH_2)(Cp_2ZrMe)_2]$ (**4**) might be a candidate.

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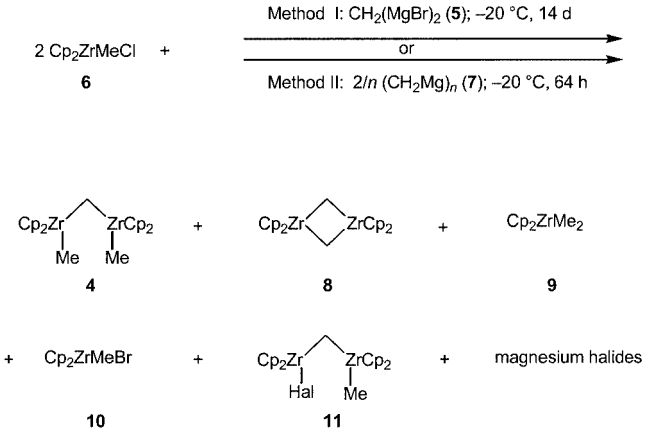
Results and Discussion

Synthesis of [(μ-CH_2)($Cp_2ZrMe)_2$] (4)

The methylene di-Grignard reagent $CH_2(MgBr)_2$ (**5**)[9−11] seemed to be a promising starting material; reaction of **5** with 2 equiv. of chloro(methyl)zirconocene (**6**)[12] is expected to yield the desired **4** (Method I, Scheme 2). Methylenemagnesium $(CH_2Mg)_n$ (**7**)[9] is potentially an alternative synthon for this purpose (Method II); originally, it was considered less attractive because it is obtained via **5**, but at a later stage **7** turned out to offer certain advantages (vide infra).



Scheme 2

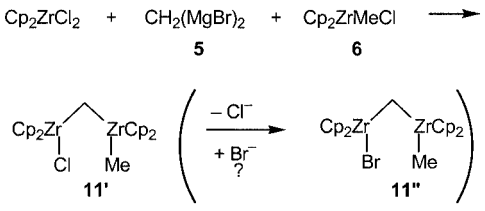
According to Method I, **5** (in benzene/diethyl ether) and **6** (in toluene) were treated at low temperatures and during longer periods. After removal of the solvents, the residue was extracted with pentane and subsequently with benzene. Table 1 shows the relative amounts of the products **4**, **8**, **9**, **10**, and **11** in the pentane and the benzene extract, respectively. The compounds were identified by ^1H NMR spectroscopy, the signals of **8**[12] and **9**[13] being in agreement with literature data, and those of **10** showing a great similarity to those of **6**. Furthermore, the structure of **4** (containing a small amount of impurity, presumably **11**) was established by X-ray crystal structure determination (vide infra).

Table 1. Formation of **4** and of by-products from **6**[a]

Reactant	Extract	**4**	**8**	**9**	**6/10**	**11**
5	pentane	16	8	37	37[b]	2
5	benzene	68	7	6	10[b]	9
7	pentane	14	14	14	53[c]	5
7	benzene	66	4	4	21[c]	5

[a] Relative amounts (%). [b] **10** only. [c] **6** + **10**.

We assume that **8** and **9** are formed by disproportionation of **4**; this reaction will be discussed later. Compound **10** is formed from **6** by halogen exchange with the bromide ion derived from **5**, while **11** probably results from the reaction of **5** with **6** and Cp_2ZrCl_2 (Scheme 3), present as an impurity in the starting material **6** (about 10%). The structural assignment of **11** as a minor side-product is only tentative and this holds, in particular, for the halogen involved. An argument for the halogen being chlorine (**11′**) might be derived from the observation (vide infra) that when the bromine-deficient **7**, instead of **5**, was treated with **6**, the chlorine atom in the latter was not fully replaced to give **10**, whereas **11** remained unchanged. Furthermore, the crystal structure analysis of **4** (vide infra) indicates the presence of (some) bromine as an impurity at this position (**11"**).



Scheme 3

From the composition of the extracts with benzene as compared to those with pentane, it is obvious that a certain degree of purification of **4** was accomplished by sequential extraction. Hydrolysis of the residues that were insoluble in both solvents, followed by titration (Mg^{2+} with EDTA and OH^- with HCl),[14] indicated that about 10% of the di-Grignard reagent **5** had not reacted. An exact determination of the yields is difficult and has not been attempted. However, from a preparative point of view, this route to **4** appears to be an attractive one, as was concluded from the results of the titration and, after evaporation of the solvent, from the visual observation that the pentane extract contained only a very small amount of material while the benzene extract, containing a substantial amount of material, consisted of nearly 70% of **4**.

The reaction of **5** with **6** was performed under a variety of conditions; a reaction temperature of −20 °C and a relatively long reaction time of 14 d appeared to provide the best results. The extraction with benzene had to be performed quickly and at 5 °C (around the melting point of benzene) because at room temperature the proportion of the side products **8** and **9** increased significantly. After the workup procedure (extraction with pentane and benzene), the extracts contained fewer magnesium salts than the original reaction mixture. This is presumably due to the low solubility of such salts in hydrocarbons, which is only slightly increased by the presence of diethyl ether; this diethyl ether is introduced with the solvent of **5** (vide supra) and successively depleted during the extraction. As disproportionation of **4** now occurred at a lower rate than before workup (**8** can be readily recognized by its red color), we speculated that magnesium halides might play a role in this disproportionation process.

To test this hypothesis, we investigated the formation of **4** from **6** and **7** (Method II), because in this case the amount of magnesium salts in the final product is strongly reduced. Unfortunately, it is not possible to obtain **7** completely bro-

mide-free.[9] The amount of residual salts depends on the intensity of extraction of $MgBr_2$ from **7** with THF, two to four extractions being a compromise between purity and yield of **7**.[9] In our case, titration after hydrolysis of **7** showed that the Mg^{2+}/OH^- ratio was 1:1.6 (instead of 1:2 as required for pure **7**), indicating a formal **7**/$MgBr_2$ ratio of 80:20 (in reality this product consists of a mixture of various oligomeric combinations of the two formal constituents).[9] Nevertheless, it is obvious that the amount of magnesium halides present after formation of **4** should be reduced considerably. Now, as expected, short periods at temperatures higher than −20 °C did not immediately lead to formation of side products; after about 10 min at 5 °C, the red color of **5** was not observed. In the product mixture, some starting material **6** was identified (^{1}H NMR spectroscopy). As **7** contained much less (magnesium) bromide than **5**, complete halogen exchange transforming **6** to **10** did not occur; instead, a mixture of both **6** and **10** was formed.

The absolute yield of **4** from **7** was determined by ^{1}H NMR spectroscopy with cyclopentane as internal standard and found to be 56% (in a ratio of 53:3 for the benzene and the pentane extract, respectively). According to ^{1}H NMR spectroscopy, **4** obtained by this procedure was converted into **8** and **9** much more slowly, confirming our assumption that magnesium halides promote the disproportionation.

Another attractive aspect of Method II is that the reaction with **7** is much faster than with **5** (64 h versus 14 d, see Scheme 2).

Structural Characterization of 4

After several attempts, yellow-orange crystals of **4**, suitable for an X-ray crystal-structure determination, were isolated from a product mixture obtained from Method II by dissolving the material in toluene/heptane (5:1) and repeated crystallizations at −80 °C. At room temperature, the crystals were quickly transferred into Lindemann glass capillaries in a glovebox under nitrogen and afterwards kept at −20 °C. The structure (**4**, crystal 1) is shown in Figure 1; selected bond lengths and angles are presented in Table 2.

A second single crystal of **4** was obtained from the reaction of **5** with **6** that was carried out in toluene (0 °C to room temperature). After workup and removal of the magnesium halides, pentane was added. From the toluene/pentane (5:2) solution bright yellow crystals of **4** were obtained at −30 °C. A second X-ray crystal structure analysis was performed with these crystals, which turned out to be of a second polymorph of **4** (**4**, crystal 2). They contained a disordered impurity that is possibly **11**′′ [$(Cp_2ZrBr)CH_2(Cp_2ZrMe)$]. Aside from this crystallographic complication, the two independent structure determinations of **4** gave practically identical results as far as the molecular structure of **4** is concerned, even though the crystal packing is completely different, as is reflected by the space group symmetry: $P2_12_12_1$ (orthorhombic) for crystal 1 versus $P\bar{1}$ (triclinic) for crystal 2. Table 2 gives a comparison of selected structural parameters of **4** obtained by these two independent X-ray crystal-structure analyses.

Table 2. Selected bond lengths and angles for **4**

	Crystal 1[a]	Crystal 2[b]	Average
Zr1−C11	2.368(3)	2.334(6)	2.351
Zr2−C23	2.294(4)	2.332(7)	−
Zr1−C12	2.225(3)	2.225(6)	2.225
Zr2−C12	2.247(3)	2.236(5)	2.242
Zr1−C12−Zr2	132.7(1)	134.0(3)	133.4
C11−Zr1−C12	101.2(1)	101.3(2)	101.3
C12−Zr2−C23	93.8(1)	92.9(2)	93.4
C11−Zr1−C12−Zr2	−0.6(3)	1.6(5)	1.1
Zr1−C12−Zr2−C23	175.7(3)	−178.7(5)	−177.2

[a] Determined in Utrecht. [b] Determined in Münster.

In the solid state, **4** is unsymmetrical. It crystallizes in an "antiperiplanar" conformation in which the methyl groups are on opposite sides of the molecule with (averaged) dihedral angles C11−Zr1−C12−Zr2 = 1.1° and Zr1−C12−Zr2−C23 = −177.2°. This specific orientation may be steric in origin, although related μ-oxozirconocene complexes usually favor a bisected (i.e. perpendicular) allene-type conformational orientation. Thus, in $[(Cp_2ZrMe)_2O]$ (**12**)[15] and related systems,[16] the Zr−O−Zr angle is close to linear [**12**: 174.1(3)°] and the Me−Zr···Zr−Me dihedral angle is close to 90°. In contrast, complex **4** favors an almost coplanar arrangement of the Zr−C σ-vectors. In the analogous and sterically rather crowded methylene-bridged complex $[(Cp^*)(C_2B_9H_{11})Zr]_2(\mu\text{-}CH_2)$ (**13**),[17] the bulky dicarbollide ligands at the zirconium atom are *trans*-oriented, too.

Of special interest is the wide bond angle at the methylene carbon atom: Zr−C12−Zr (133.4°). While the geometry around C12 is clearly not planar, it shows a pro-

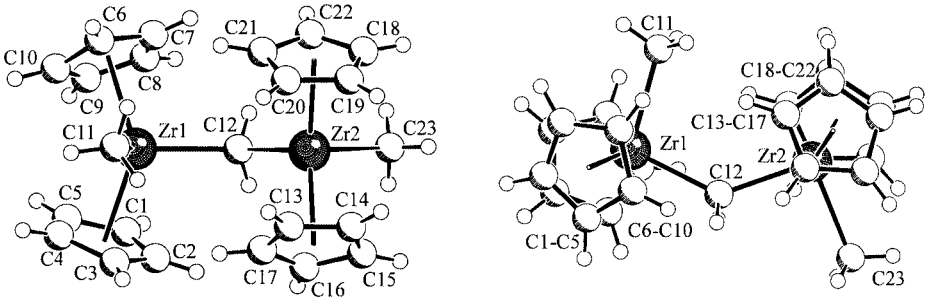


Figure 1. Two views of the molecular structure of **4** (crystal 1)

nounced tendency of flattening in the direction of D_{2h} symmetry. This may be compared with several related structures. Compound **3**[7] has a much smaller Zr1−C1−Zr2 angle [101.86(10)°], but this is due to the fact that it is incorporated into a four-membered ring (involving a chlorine atom); in this case, it is the external angle Zr2−C1−C2 [145.9 (2)°] that is opened up. In **13**, the angles around the methylene carbon atom are rather normal [Zr−CH_2−Zr (119.14°) and H−C−H (108.74°)]; the Zr−CH_2 bond lengths [2.187(6) and 2.176(7) Å] are slightly shorter than those in **4** (2.225 and 2.242 Å). These shorter bonds may signal more s-character in the Zr−CH_2 bond of **13**, although a stabilizing bridging Zr···H−B interaction has also been considered.[17] The wider bond angles in **4** might also be considered as indicators for more s-contribution to the Zr−CH_2 bonds. Apparently, a number of different effects with a complicated interplay are involved. The Zr−CH_3 σ-bonds are in the expected range (see Table 2).[15,17] It must be noted, however, that the Zr1/2−C12 linkages are different from each other. While the Zr2−C12 bond (average 2.242 Å) is in the typical range for zirconium−carbon σ-bonds, the Zr1−C12 bond is shorter at (averaged) 2.225 Å. The latter value is close to the Zr−CH_2 bond lengths observed in the (μ-methylene)zirconocene system **13**.[17] The Zr−C(Cp) bond lengths of **4** lie in a range between 2.491 and 2.570 Å.

In general, the NMR spectroscopic data (Table 3) are in line with the crystal structure. A major difference is that, in solution, the structure is symmetrical, as the two methyl groups and the four cyclopentadienyl groups show only one signal each. Even at −100 °C, only one signal is observed for the methyl groups, which means that the conformational equilibrium in **4** has a very low barrier.

Table 3. NMR spectroscopic data for **4** (δ in ppm)

Group	δ(^{1}H)[a]	δ(^{1}H)[b]	δ(^{13}C)[a]	δ(^{13}C)[b]
Cp	5.73	6.11	109.1 (170.7)[c]	109.8 (171.5)[c]
CH_2	3.68	3.76	146.4 (107.2)[c]	145.8 (106.5)[c]
CH_3	−0.32	−0.46	22.5 (115.9)[c]	22.0 (117.6)[c]

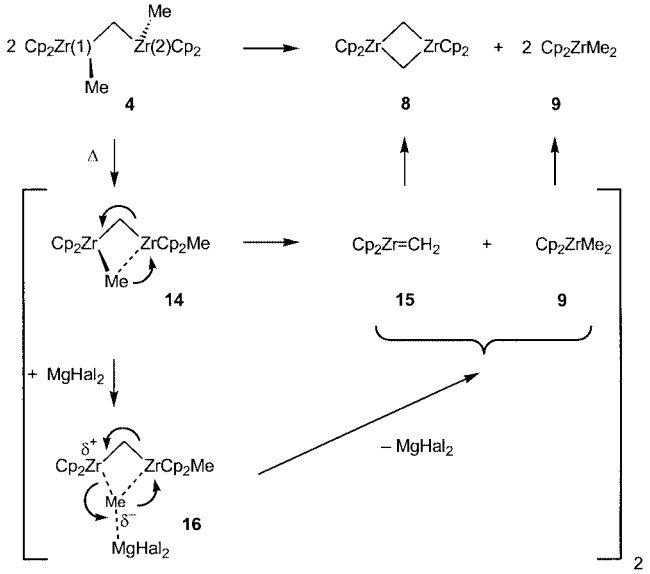
[a] In [D_8]toluene. [b] In [D_8]THF. [c] $^1J_{C,H}$ [Hz] in parentheses.

The deshielded ^{13}C NMR chemical shift of δ= 146 ppm and the small $^1J_{C,H}$ coupling constant of 107 Hz are typical for a methylene group bridging between two metal atoms. Methylene groups in 1,3-dimetallacyclobutanes are even more deshielded,[10,18] as exemplified by the value of δ = 173 ppm for **8**. For methylene groups bridging between two transition metal atoms, such as manganese or rhodium, metal−metal bonding has been invoked,[18] but in **4**, the Zr−Zr distance of 4.10 Å clearly excludes such interactions, as the Zr−Zr distance in the metal is 3.2 Å.[19]

As discussed above, the large Zr−CH_2−Zr angle of 133.4° may be an indication of a relatively high s-character of these bonds, which facilitates the accommodation of electron density released from the metal atoms towards the carbon atom. As a consequence, less s-character is left for the C−H bonds, which explains the small $^1J_{C,H}$ value of 107 Hz (cf. $^1J_{C,H}$ = 117 Hz for the methyl groups) because in the latter, the carbon atom is bonded to only *one* metal atom.

Thermal Disproportionation of 4

In order to further investigate the disproportionation of **4** to **8** and **9**, as mentioned above, the benzene extract of a mixture obtained by Method I containing approximately 70% of **4** was subjected to a kinetic analysis. For this purpose, the solution was kept at 5 °C (cold room) while the solvent was removed by distillation under vacuum into a vessel cooled by liquid nitrogen, followed by high-vacuum pumping. A sample of the residue was dissolved in [D_8]toluene and transferred into an NMR tube, which was subsequently sealed. In the NMR spectrometer, the tube was warmed to 55 °C and the ^{1}H NMR spectrum was recorded. As determination of the absolute concentration of the components was not possible, their relative concentration was derived from the ratio between the intensity of their signals (per proton) and that of the solvent. The sum of the integrals of all cyclopentadienyl signals remained unchanged, which means that decomposition to insoluble products had not occurred. Taking into account the low initial concentrations of **8** and **9** formed during the synthesis of **4** (see Table 1), the two products were newly formed in a ratio of 1:2 as required by stoichiometry (Scheme 4).



Scheme 4

The disproportionation of **4** follows roughly first-order kinetics with $k = 19 \times 10^{-5}$ s^{-1}. A conceivable mechanism is presented in Scheme 4. In the transition state, **14**, of the first and rate-determining step, a methyl group migrates from Zr1 to Zr2, while, simultaneously, the Zr2−CH_2 bond starts to cleave. This produces **9** and the carbene complex **15** which, being highly unstable, immediately dimerizes to form **8**. However, several observations suggest that this

mechanism may be too simple. In the first place, it does not explain the strong influence of magnesium salts mentioned above. Secondly, when an identical sample of **4** obtained by Method I was dissolved in [D_8]THF instead of [D_8]toluene, the stability increased considerably: at 55 °C, only a small percentage of **4** had undergone disproportion after 64 h, and after 9.5 months at room temperature, the intensity of the signals of **4** had decreased by only 35%. This may be tentatively explained by the strong coordination of $MgHal_2$ by THF, which "inactivates" the salt.

This is supported by two other experiments with a sample of **4** that had been purified and made (practically) salt-free by repeated crystallization from toluene/heptane (5:1), followed by ^{1}H NMR spectroscopy in [D_8]toluene. After heating the solution at 60 °C, 50% of **4** had survived after one month; again, kinetic order (first order) and product formation (**8**/**9** = 1:2) were unchanged. However, when an excess of $MgBr_2$ was added to this salt-free toluene solution, disproportionation occurred within a few hours, although in this case product formation was less straightforward: initially, signals of **9** and **10** were observed while those of **8** appeared only later and in a ratio smaller than 1:2; in addition, unidentified products were formed (singlets at δ = 5.78, 5.76, 0.30, −0.10 ppm).

Thus, it is obvious that magnesium salts do play an important role. From the fact that the reaction is of first order, it follows that they act as catalysts; a tentative rationalization is shown in Scheme 4. One can imagine that in an apolar medium, $MgHal_2$ coordinates to **4**, presumably at the "external" methyl group at Zr1 (Figure 1) as shown in **16**. This will accelerate the cleavage of the Me−Zr2 bond and thus promote migration of the methyl group and the ensuing cleavage process.

Cation Formation

Dimethylzirconocene reacts with the strong Lewis acid $B(C_6F_5)_3$ and a variety of related reagents with abstraction of a methyl anion equivalent to form the respective methylzirconocene cation.[20] A similar reaction was observed when **4** was treated with $B(C_6F_5)_3$ in dichloromethane at low temperature: a methyl group was transferred from a zirconium to a boron atom to yield **17** (Scheme 5). The dimetallic cation of **17** is characterized by a single Cp resonance in the ^{1}H NMR spectrum at δ = 6.60 ppm, integrating for 20 protons (δ(^{13}C) = 114.5 ppm), in addition to ^{1}H NMR resonances of the CH_2 group at δ = 8.01 ppm (**4**: δ = 3.77 ppm) and of the bridging methyl group at δ = −1.05 ppm. The ^{13}C NMR methylene resonance is markedly different from that of its neutral precursor **4** [**17**: δ = 186.6 ppm ($^1J_{C,H}$ = 124 Hz); **4**: δ = 145.1 ppm ($^1J_{C,H}$ = 107 Hz)]. The ^{13}C NMR resonance of the bridging CH_3 group of **17** occurs at δ = 47.4 ppm [$^1J_{C,H}$ = 109 Hz; cf. δ = 22.7 ppm ($^1J_{C,H}$ = 118 Hz) for **4**].

Complex **17** is not stable in dichloromethane solution for a prolonged time at ambient temperature as it reacts with this solvent to yield the chloride-bridged complex **18**. On a preparative scale, it was synthesized by treatment of **17** with trityl chloride to cleanly furnish **18** [CH_2: δ(^{1}H) = 8.53 ppm; δ(^{13}C) = 193.7 ppm ($^1J_{C,H}$ = 124 Hz)] and 1,1,1-triphenylethane. Single crystals of **18** were obtained from a concentrated CD_2Cl_2 solution in an NMR tube. The X-ray crystal structure analysis (Figure 2) shows the formation of the four-membered metallacycle, although a 1:1 disorder of the μ-Cl and μ-CH_2 groups allows the calculation of average Zr−Cl/CH_2 bond lengths and angles only inside the framework of **18**.

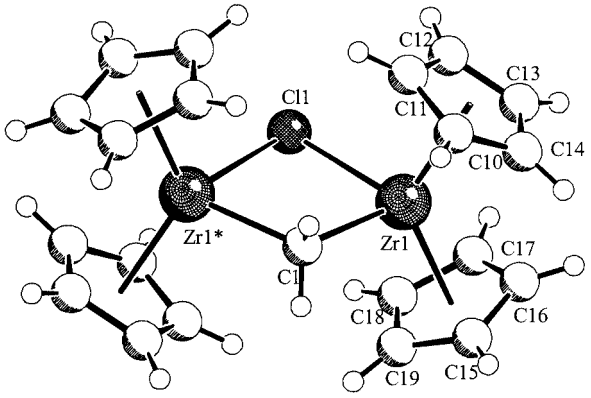
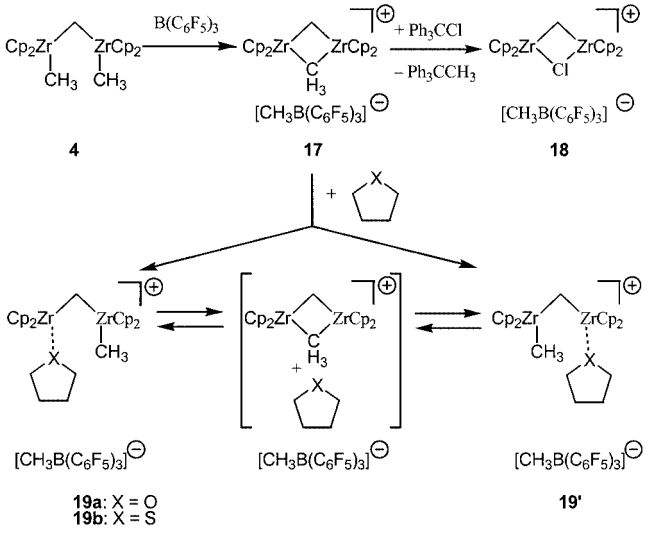


Figure 2. View of the molecular structure of **18** (the counterion has been omitted for clarity)

The addition of 1 equiv. of tetrahydrofuran to **17** opens the μ-CH_3 bridge with formation of the unsymmetrically substituted (μ-methylene)dizirconocene cation **19a** [μ-CH_2: δ(^{1}H) = 5.13 ppm; δ(^{13}C) = 163.4 ppm ($^1J_{C,H}$ = 106 Hz); Scheme 5]. The THF-stabilized cation shows dynamic NMR spectra. At room temperature and above it exhibits a single Cp resonance (in CD_2Cl_2, 600 MHz) which decoalesces below 280 K into an equal intensity pair of C_5H_5 singlets (δ = 6.38 and 6.17 ppm at 218 K). This probably indicates a process where THF is readily removed from the dinuclear complex to re-form the C_s-symmetric methyl-bridged cation **17**. Attack of THF can then occur at either side of the dimetallic complex, which leads to the observed



Scheme 5

equilibration process (Scheme 5). From the dynamic ^1H NMR spectra of **19a**, a Gibbs activation energy of $\Delta G^{\neq}(280\ K) = 13.1 \pm 0.5$ kcal mol^{-1} was estimated.

Tetrahydrothiophene (THT) reacts similarly with **17** to form the unsymmetrical THT adduct **19b** (Scheme 5). It shows a pair of Cp ligand signals (1:1 intensity) at very low temperature in CD_2Cl_2 (193 K: $\delta(^1H)$ = 6.35, 6.17 ppm; $\delta(^{13}C)$ = 111.5, 110.5 ppm) in addition to a μ-CH_3 singlet at $\delta(^1H) = -0.53$ ppm ($\delta(^{13}C)$ = 10.2 ppm) and a μ-CH_2 resonance at $\delta(^1H)$ = 5.59 ppm and $\delta(^{13}C)$ = 169.2 ppm ($^1J_{C,H}$ = 107 Hz) in addition to the THT ligand and the $[CH_3B(C_6F_5)_3]^-$ anion resonances. Warming of the sample in the NMR spectrometer rapidly leads to coalescence of the Cp signals. From the dynamic ^1H NMR spectra a barrier of $\Delta G^{\neq}(213\ K) = 9.9 \pm 0.5$ kcal mol^{-1} was obtained for the dynamic equilibration process of **19b**.

Conclusion

The title compound [(μ-CH_2)($Cp_2ZrMe)_2$] (**4**) was obtained from [$Cp_2Zr(Cl)Me$] (**6**) and the two methylenedimagnesium reagents $CH_2(MgBr)_2$ (**5**) or $(CH_2Mg)_n$ (**7**). The X-ray crystal structure of **4** showed that the carbon atom of the central methylene group is non-planar, but a widened Zr−C−Zr angle of 133.4° indicates the tendency of this carbon atom to become planar. On first inspection, **4** may just be regarded as a methane derivative where the central methylene group bears two very bulky (Cp_2ZrMe) substituents. These have a tendency to become oriented far away from each other, thereby leading to an increased metal−CH_2−metal angle.

However, there are some noteworthy features of **4** which may be caused by factors other than simply by steric strain. Planarization of methane derivatives eventually would result in a transition from sp^3- to sp^2-hybridization of the central carbon atom.[2] By this type of re-hybridization, a doubly occupied p-orbital would develop which is oriented perpendicular to the plane of the σ-bonds. One must note that in complex **4** the electrophilic Cp_2ZrCH_3 substituents are both oriented such that their available acceptor orbitals[21] could, in principle, interact with this developing p-orbital at the bridging carbon atom and potentially stabilize it. In the observed unsymmetrical situation, it appears that the metallocene group at Zr1 (see Figure 1) could just have started to profit from such a developing electronic interaction. This might be the reason why the corresponding Zr1−C12 bond is slightly shorter than its adjacent Zr2−C12 neighbor. This is probably only a small energetic effect, but it seems that **4** represents a system where the bonding features of the central methylene carbon atom are just in the initial stage of being distorted from the common pseudo-tetrahedral coordination environment of tetracoordinate carbon toward its unusual planar-tetracoordinate isomer. This unusual structural feature may actually bear some relevance to its chemical behavior: **4** turned out to be relatively stable in THF solution, but it disproportionates in toluene solution to give the 1,3-dizirconacyclobutane [($Cp_2ZrCH_2)_2$] (**8**) and dimethylzirconocene [Cp_2ZrMe_2] (**9**). This reaction appears to be catalyzed by magnesium salts.

Reaction of **4** with $B(C_6F_5)_3$ yielded the methyl-bridged cationic complex **17** which, on treatment with trityl chloride, was transformed into the corresponding chloro complex **18**. The latter has been characterized by X-ray crystal structure determination. With THF and tetrahydrothiophene, **17** formed the adducts **19a** and **19b**, respectively, which are unsymmetrical in solution at low temperatures.

Experimental Section

General Remarks: Most of the experiments were performed using a high-vacuum sealed-glass apparatus,[11,14] in Schlenk-type glassware or in a glove box. Solvents were dried before use by distillation from liquid NaK alloy under argon. Magnesium was triply sublimed. For the determination of some NMR spectra, the solution obtained from a reaction was concentrated to dryness by distilling off the solvent under vacuum into a vessel cooled by liquid nitrogen, followed by pumping under high vacuum; subsequently, the sample was redissolved in a deuterated solvent in a high vacuum system and finally the NMR tube was sealed. NMR spectra were measured with a Bruker WH 90, AC 200, WM 250 or a Varian Unity Plus (^1H: 600 MHz) spectrometer. GCMS analysis was performed with a Hewlett Packard 5890 GC/5970 MS combination with a 50-m Chrompack CP Sil 5 column.

X-ray Crystal-Structure Determinations

4 (Crystal 1): Data collection by locally modified CAD4 software (*CAD-4 Software*, version 5, Enraf−Nonius, Delft, The Netherlands, **1989**); structure solution: SHELXS-86 (G. M. Sheldrick, *SHELXS-86, Program for Crystal Structure Solution*, University of Göttingen, Germany, **1986**); structure refinement: SHELX-76 (G. M. Sheldrick, *SHELX-76, Program for crystal structure solution and refinement*; University of Göttingen, Germany, **1976**); graphics PLATON (A. L. Spek, *PLATON, A multi-purpose crystallographic tool*, Utrecht University, The Netherlands, 2003, internet: http://www.cryst.chem.uu.nl/platon/).

4 (Crystal 2) and 18: Data sets were collected with an Enraf Nonius CAD4 diffractometer. Programs used: data collection EXPRESS (Nonius B.V., **1994**), data reduction MolEN (K. Fair, Enraf−Nonius B.V., **1990**), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, **1997**), graphics SCHAKAL (E. Keller, Universität Freiburg, **1997**).

CCDC-221605 (**4**, crystal 1), -221381 (**4**, crystal 2) and -221380 (**18**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

(μ-Methylene)bis[dicyclopentadienyl(methyl)zirconium] (4)

Method I: At −20 °C, a solution of **6**[12] (185.2 mg, 0.68 mmol) in toluene (20 mL) was added to a solution of **5** (0.34 mmol) in diethyl ether/benzene (1:1; 12.4 mL). The reaction mixture was stirred at −20 °C for 14 d, after which time the mixture had become yellow-orange and homogeneous. The solution was kept at 5 °C (cold room) while the solvent was removed by distillation under vacuum

into a vessel cooled by liquid nitrogen followed by high vacuum pumping, and the solid residue was extracted with pentane (10 mL, 5 times) and benzene (10 mL), and filtered. Hydrolysis and titration[11] of the residue in the reaction vessel showed that about 10% of **5** had not reacted (a small part may be lost during the workup procedure as well). Titration with EDTA revealed that some of the magnesium salts dissolved in the benzene extract. The yield of **4** was about 60% as determined by ^{1}H NMR spectroscopy with cyclopentane as internal standard. The ratios of products in the pentane and in the benzene extract are reported in Table 1. The NMR spectroscopic data for **4** are presented in Table 3. ^{1}H NMR spectroscopic data for by-products (200 MHz, [D_8]toluene, reference [D_7]toluene at δ = 2.03 ppm). **8:** δ = 6.27 (s, 4 H, CH_2), 6.09 (s, 20 H, Cp) ppm; the data are in agreement with those reported previously.[10] **9:** δ = 5.64 (s, 10 H, Cp), −0.25 (s, 6 H, Me) ppm; the data are similar to those reported previously.[13] **10:** δ = 5.68 (s, 10 H, Cp), 0.15 (s, 3 H, Me) ppm. **11:** δ = 5.89 (s, 10 H, Cp), 5.82 (s, 10 H, Cp), 4.37 (s, 2 H, CH_2), −0.15 (s, 3 H, Me) ppm.

Method II: At −20 °C, a solution of **6** (92.9 mg, 0.34 mmol) in toluene (10 mL) was added to a suspension of **7**[9,11] (0.17 mmol of **7**; see general text for the composition of the reagent) in THF (6.2 mL). The mixture was stirred at −20 °C for 64 h; this was followed by stirring at 5 °C for 2 h and at room temperature for 2 h while the solvents were removed by distillation under vacuum into a vessel cooled by liquid nitrogen followed by high vacuum pumping. The reaction vessel was evacuated at room temperature for 2 h. At room temperature, the residue was extracted with pentane (10 mL), filtered, and subsequently extracted with benzene (10 mL). Analysis by ^{1}H NMR spectroscopy with cyclopentane as internal standard showed that the total yield of **4** was 56% (53% in the benzene extract; 3% in the pentane extract). The composition of the extracts is reported in Table 1. Compound **4** was purified by crystallization from a toluene/heptane (5:1) solution at −80 °C. At room temperature, the crystals were quickly transferred into Lindemann capillaries in a glove box under nitrogen and afterwards kept at −20 °C.

X-ray Crystal Structure of 4 (Crystal 1): $C_{23}H_{28}Zr_2$, M_r = 486.91, orange crystal, 0.2 × 0.2 × 0.3 mm, orthorhombic, space group $P2_12_12_1$ (no. 19) with a = 10.0234(14), b = 13.8914(6), c = 14.3841(18) Å, V = 2002.8(4) Å^3, Z = 4, $\rho_{calcd.}$ = 1.615 g cm^{-3}, $F(000)$ = 984, $\mu_{Mo\text{-}K\alpha}$ = 1.03 mm^{-1}. 6884 reflections measured with an Enraf−Nonius CAD4-T diffractometer with a rotating anode ($\lambda_{Mo\text{-}K\alpha}$ = 0.71073 Å, T = 100 K, θ_{max} = 34.9°), 6358 unique (R_{int} = 0.027), 5063 observed [$I > 2.5\sigma(I)$]. Structure solved with SHELXS-86. 305 parameters refined with SHELX-76, R = 0.0355, R_w = 0.0358, S = 1.61, residual density in the range −1.00, 1.40 e$^-$/Å^3. Hydrogen atom coordinates, with exception of the methyl moieties, were refined. The low value of the displacement parameters of methyl group C11 in comparison with the other methyl group might be explained as substitutional disorder with Br. However, no satisfactory disorder model could be refined, suggesting that, if any, only a very small fraction of Br is present.

Method III: The single crystals used for the X-ray crystal structure analysis in Münster (Table 2, crystal 2) were obtained as follows: A solution of **6** (0.63 g, 2.32 mmol) in toluene (10 mL) was cooled to 0 °C. Then, a solution of **5** [diethyl ether/benzene (1:1), 50 mL, 0.025 M, 1.25 mmol of **5**) was added. The ice bath was removed and the mixture stirred at room temperature for 1 h. Dioxane (2.5 mL) was added and the mixture stirred for 15 min. The solvent was then removed in vacuo. The residue was suspended in toluene (15 mL), the magnesium halide precipitate was removed by filtration, and the clear solution concentrated to about 5 mL. Pentane (2 mL) was added and the solution cooled to −30 °C to yield bright yellow crystals of **4** (0.37 g, 65%).

X-ray Crystal-Structure Analysis of 4 (Crystal 2): $C_{23}H_{28}Zr_2{\cdot}1/2$ correctly represents composition of crystal ($C_{22.86}H_{27.58}Br_{0.14}Zr_2$), M = 734.88, yellow crystal 0.40 × 0.40 × 0.05 mm, a = 10.787(1), b = 13.028(1), c = 13.066(1) Å, α = 63.55(1), β = 69.77(1), γ = 80.83(1)°, V = 1542.6(2) Å^3, $\rho_{calcd.}$ = 1.582 g cm^{-3}, μ = 11.06 cm^{-1}, empirical absorption correction with ψ-scan data (0.666 ≤ T ≤ 0.947), Z = 2, triclinic, space group $P\bar{1}$ (no. 2), λ = 0.71073 Å, T = 223 K, ω/2θ scans, 6565 reflections collected (±h, +k, ±l), [(sinθ)/λ] = 0.62 Å^{-1}, 6275 independent (R_{int} = 0.031) and 4199 observed reflections [$I \geq 2\sigma(I)$], 356 refined parameters, R = 0.049, wR^2 = 0.129, max. residual electron density 0.68 (−1.20) e$^-$/Å^3, hydrogen atoms calculated and refined as riding atoms, in the second independent molecule 7% of the terminal CH_3 group is substituted by Br, in addition the bridging CH_2 group is split over two positions due to symmetry.

Synthesis of 17: Solid **4** (120 mg, 0.25 mmol) was mixed with solid $B(C_6F_5)_3$ (126 mg, 0.25 mmol). Toluene (10 mL) was then slowly added at −78 °C. The mixture was stirred at −78 °C for 20 min and then allowed to warm to room temperature. The toluene phase was decanted from the precipitated oil. The remaining product was washed twice with pentane to give **17** as a yellow powder (70 mg, 28%). $C_{41}H_{28}BF_{15}Zr_2$ (998.9): calcd. C 49.30, H 2.83; found C 48.72, H 3.04. ^{1}H NMR (CD_2Cl_2, 360 MHz, 213 K): δ = 8.01 (s, 2 H, CH_2), 6.60 (s, 20 H, Cp), 0.36 (br., 3 H, CH_3−[B]), −1.05 (s, 3 H, Zr−CH_3) ppm. ^{13}C NMR (CD_2Cl_2, 90.6 MHz, 213 K): δ = 186.6 (t, $^1J_{C,H}$ = 124 Hz, CH_2), 147.4 [d, $^1J_{C,F}$ = 236 Hz, *o*-$B(C_6F_5)_3$], 136.4 [d, $^1J_{C,F}$ = 246 Hz, *p*-$B(C_6F_5)_3$], 135.5 [d, $^1J_{C,F}$ = 243 Hz, *m*-$B(C_6F_5)_3$], 127.8 [s, *ipso*-$B(C_6F_5)_3$], 114.5 (d, $^1J_{C,H}$ = 174 Hz, Cp), 47.4 (q, $^1J_{C,H}$ = 109 Hz, μ-CH_3), 9.2 (br., CH_3−[B]) ppm.

Synthesis of 18

Method I: A solution of $B(C_6F_5)_3$ (0.14 g, 2.74 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of **4** (0.14 g, 2.90 mmol) in CH_2Cl_2 (15 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 2 h and then at room temperature for 12 h. Pentane (5 mL) was then added. Cooling to −45 °C gave a red precipitate that was isolated and dried in vacuo to yield **18** (55 mg, 19%). ^{1}H NMR (CD_2Cl_2, 360 MHz, 300 K): δ = 8.53 (s, 2 H, CH_2), 6.69 (s, 20 H, Cp), 0.49 (br., 3 H, CH_3−[B]) ppm. ^{11}B NMR (CD_2Cl_2, 64.2 MHz, 300 K): δ = −15.1 ppm. ^{13}C NMR (CD_2Cl_2, 90.6 MHz, 300 K): δ = 193.5 (t, $^1J_{C,H}$ = 124 Hz, CH_2), 148.0 [d, $^1J_{C,F}$ = 233 Hz, *o*-$B(C_6F_5)_3$], 138.9 [d, $^1J_{C,F}$ = 246 Hz, *p*-$B(C_6F_5)_3$], 136.1 [d, $^1J_{C,F}$ = 242 Hz, *m*-$B(C_6F_5)_3$], 129.3 [s, *ipso*-$B(C_6F_5)_3$], 115.5 (d, $^1J_{C,H}$ = 175 Hz, Cp), 11.7 (br., CH_3−[B]) ppm. ^{19}F NMR (CD_2Cl_2, 282.2 MHz, 300 K): δ = −126.1, −162.9, −165.4 [*o*-, *p*-, *m*-$B(C_6F_5)_3$] ppm. Single crystals of **18** were obtained by slow evaporation of the solvent from a solution of the complex in CD_2Cl_2.

X-ray Crystal-Structure Analysis of 18: $C_{21}H_{22}ClZr_2{\cdot}CH_3B(C_6F_5)_3$, M = 1019.30, red crystal 0.40 × 0.25 × 0.15 mm, a = 10.768(1), b = 11.305(1), c = 16.283(1) Å, α = 71.93(1), β = 86.31(1), γ = 88.91(1)°, V = 1880.5(3) Å^3, ρ = 1.800 g cm^{-3}, μ = 7.31 cm^{-1}, empirical absorption correction with ψ-scan data (0.759 ≤ T ≤ 0.898), Z = 2, triclinic, space group $P\bar{1}$ (no. 2), λ = 0.71073 Å, T = 223 K, ω/2θ scans, 6979 reflections collected (±h, −k, ±l), [(sinθ)/λ] = 0.59 Å^{-1}, 6612 independent (R_{int} = 0.033) and 3880 observed reflections [$I \geq 2\sigma(I)$], 551 refined parameters, R = 0.038, wR^2 = 0.071, max. residual electron density 0.59 (−0.41) e$^-$/Å^3, hydrogen atoms calculated and refined as riding atoms, the bridg-

ing CH_2 and Cl groups are split over two positions due to symmetry.

Method II: Complex **4** (50 mg, 0.10 mmol) was mixed with solid $B(C_6F_5)_3$ (53 mg, 0.10 mmol). Toluene (10 mL) was added slowly at −78 °C. The mixture was stirred at −78 °C for 20 min. A precooled solution (−78 °C) of trityl chloride (30 mg, 0.10 mmol) in toluene (10 mL) was then added. The mixture was warmed to room temperature and then stirred for another 10 min. The toluene phase was separated from the precipitated oil of the organometallic product **18** (see above) and washed twice with pentane. From the combined organic phases 1,1,1-triphenylethane[22] was recovered as a white powder (34 mg 35%). M.p. 95 °C.

Reaction of 17 with THF

Formation of 19a: Compound **4** (20 mg, 41 μmol) was dissolved in 0.5 mL of CD_2Cl_2. A solution of $B(C_6F_5)_3$ (21 mg, 41 μmol) in CD_2Cl_2 (0.5 mL) was added at −78 °C. After 10 min, THF (3 mg, 43 μmol) in $CD_2Cl_2$was added. The solution was flame-sealed in an NMR tube and the temperature-dependent NMR spectra of the resulting complex **19a** were recorded. ^{1}H NMR (600 MHz, CD_2Cl_2, 218 K): δ = 6.38 (s, 10 H, Cp), 6.17 (s, 10 H, Cp), 5.34 (s, 2 H, CH_2), 3.58 (m, THF), 1.61 (m, THF), 0.42 (br., 3 H, CH_3−[B]), −0.43 (s, 3 H, Zr−CH_3) ppm. ^{1}H NMR (600 MHz, CD_2Cl_2, 300 K): δ = 6.34 (s, 20 H, Cp), 5.13 (s, 2 H, CH_2), 3.58 (m, THF), 1.69 (m, THF), 0.62 (br., 3 H, CH_3−[B]), −0.22 (s, 3 H, Zr−CH_3) ppm. Coalescence of the Cp signals at 280 K, Δν (at the limiting low temperature) is 126 Hz, $\Delta G^{\neq}$ (280 K) = 13.1 ± 0.5 kcal mol^{-1}. ^{13}C NMR (150.6 MHz, [D$_8$]THF, 218 K): δ = 163.4 (t, $^1J_{C,H}$ = 106 Hz, CH_2), 150.4 [d, $^1J_{C,F}$ = 236 Hz, *o*-$B(C_6F_5)_3$], 138.4 [d, $^1J_{C,F}$ = 246 Hz, *p*-$B(C_6F_5)_3$], 136.8 [d, $^1J_{C,F}$ = 243 Hz, *m*-$B(C_6F_5)_3$], 130.8 [s, *ipso*-$B(C_6F_5)_3$], 117.5 (d, $^1J_{C,H}$ = 174 Hz, Cp), 114.5 (d, $^1J_{C,H}$ = 174 Hz, Cp), 43.5 (q, $^1J_{C,H}$ = 122 Hz, Zr-CH_3), 11.2 (br., CH_3−[B]) ppm.

Reaction of 17 with Tetrahydrothiophene (THT)

Formation of 19b: As described above, **4** (40 mg, 82 μmol) was treated in CD_2Cl_2 first with $B(C_6F_5)_3$ (42 mg, 82 μmol) and then with tetrahydrothiophene (7 mg, 85 μmol) at −78 °C to form **19b**. A sample of the solution was flame-sealed in an NMR tube for spectroscopic characterization. ^{1}H NMR (600 MHz, CD_2Cl_2, 183 K): δ = 6.35 (s, 10 H, Cp), 6.17 (s, 10 H, Cp), 5.59 (s, 2 H, CH_2), 3.08 (br., free THT), 2.82 (br., coordin. THT), 1.83 (br., coordin. THT), 1.68 (br., free THT), 0.40 (br., 3 H, CH_3−[B]), −0.53 (s, 3 H, Zr−CH_3) ppm. ^{1}H NMR (600 MHz, CD_2Cl_2, 300 K): δ = 6.29 (s, 20 H, Cp), 5.59 (s, 2 H, CH_2), 3.02 (m, THT), 1.87 (m, THT), 0.41 (br., 3 H, CH_3−[B]), −0.50 (s, 3 H, Zr−CH_3) ppm. Coalescence of the Cp signals at 213 K, Δν (lower limit) = 109 Hz, $\Delta G^{\neq}$ (213 K) = 9.9 ± 0.5 kcal mol^{-1}. ^{13}C NMR (150.6 MHz, CD_2Cl_2, 183 K): δ = 169.2 (t, $^1J_{C,H}$ = 107 Hz, CH_2), 147.5 [d, $^1J_{C,F}$ = 237 Hz, *o*-$B(C_6F_5)_3$], 137.5 [d, $^1J_{C,F}$ = 246 Hz, *p*-$B(C_6F_5)_3$], 135.5 [d, $^1J_{C,F}$ = 243 Hz, *m*-$B(C_6F_5)_3$], 127.8 [s, *ipso*-$B(C_6F_5)_3$], 111.5 (d, $^1J_{C,H}$ = 175 Hz, Cp), 110.5 (d, $^1J_{C,H}$ = 175 Hz, Cp), 42.5 (m, α-THT), 32.5 (m, β-THT), 26.5 (q, $^1J_{C,H}$ = 110 Hz, Zr−CH_3), 10.2 (br., CH_3−[B]) ppm.

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