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Journal of Organometallic Chemistry 569 (1998) 217–223

Journal of Organo metallic Chemistry

Addition of Group 4 bent metallocene cation complexes to (butadiene)zirconocene: the formation of dinuclear (μ-butadiene)bis(metallocene) cations[1]

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Received 14 May 1998

Abstract

Methylzirconocene cation [$Cp_2ZrCH_3^+$] (**2**) adds readily to (butadiene)zirconocene to yield the dimetallic cationic complex [(Cp_2Zr)(μ-CH_3)(μ-butadiene)($ZrCp_2$)$^+$] (**4**) (both cations with $CH_3B(C_6F_5)_3^-$ (**a**) or $B(C_6F_5)_4^-$ (**b**) counteranion). The spectroscopic analysis indicates the presence of a C_2-symmetrical bridging mode of the transoid μ-η^2:η^2-conjugated diene ligand. Treatment of **4a** with $Cp_2Zr(CH_3)Cl$ results in the formation of the μ-chloro-bridged system [$(Cp_2Zr)_2$(μ-Cl)(μ-C_4H_6)$^+$] (**4d**), that yields [$(Cp_2Zr)_2$(μ-C≡C–CH_3)(μ-C_4H_6)$^+$] (**4e**) upon treatment with propynyl lithium. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Group 4 metallocene; Zirconocene cation comnplex; Butadiene metal complex

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1. Introduction

Alkylzirconocene cations have become of a great importance recently, mostly due to their involvement as the active species in homogeneous Ziegler–Natta-catalysis [1]. In addition Cp_2ZrR^+ species, with varying groups R, have been increasingly useful as stoichiometric reagents in organometallic synthesis [2]. Due to their strongly electrophilic nature, the Cp_2ZrR^+ complexes exhibit a pronounced tendency to undergo addition reactions that lead to an increased co-ordinative saturation. In the gas phase this is most readily achieved by forming intramolecular 'agostic' interactions with adjacent carbon–hydrogen bonds [3]. In the condensed phase ion pairing with the respective counteranion is an often observed mode of (reversible) stabilization [4], as is the addition of co-ordinating solvent molecules such as e.g. tetrahydrofuran [5]. Bochmann has recently shown that the addition of neutral weakly nucleophilic organometallic reagents to Cp_2ZrR^+ systems is a very favorable reaction mode. A typical example is the facile reaction of $Cp_2ZrCH_3^+$ with the neutral $Cp_2Zr(CH_3)_2$ complex, that has served as its direct synthetic precursor, to form the cationic dinuclear μ-methyl bridged complex [$Cp_2Zr(CH_3)$-(μ-CH_3)-$Zr(CH_3)Cp_2$]$^+$ [6].

We had shown in a number of studies that (η^4-butadiene)zirconocene [7] adds a large variety of electrophilic organic and organometallic reagents very selectively to the conjugated diene ligand to form various novel types of organometallic systems [8], some of which were shown to be useful in organic synthesis [9], and others have turned out to be interesting new catalyst systems [10]. Therefore, it was likely that the (η^4-butadiene)zirconocene reagent could also be used for

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[1] Dedicated to Professor Akira Nakamura on the occasion of his retirement.

PII S0022-328X(98)00790-6

trapping the non-stabilized, reactive Cp_2ZrR^+ cation systems, and thus open up a synthetic pathway to novel cationic (μ-conjugated diene) Group 4 metal complexes. Treatment of $Cp_2Zr(CH_3)^+$ with (butadiene)zirconocene indeed led to the expected adduct formation, and to the disclosure of some interesting reactions of the obtained dinuclear [(μ-conjugated diene)(μ-X)$(ZrCp_2)_2]^+$ cationic systems. First examples of the organometallic chemistry of such systems are described in this article.

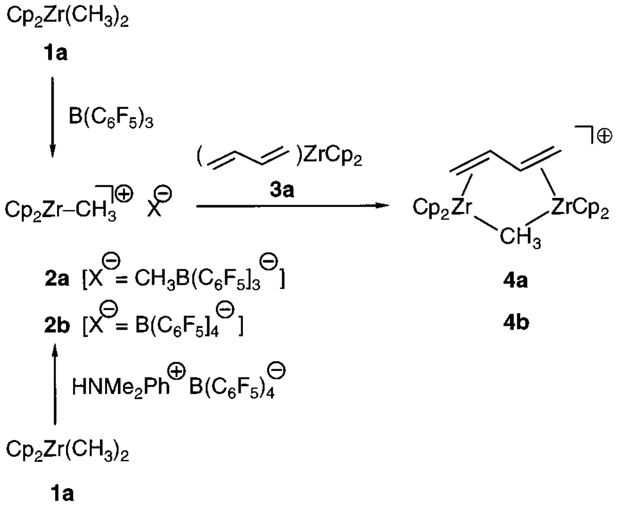
2. Results and discussion

We have generated the organometallic salt $[Cp_2Zr(CH_3)^+CH_3B(C_6F_5)_3^-]$ **2a** in a non-coordinating solvent by treatment of dimethyl zirconocene (**1a**) with tris(pentafluorophenyl)borane in toluene, as described in the literature ([4]a). A clear solution of **2a** is obtained, to which the (butadiene)zirconocene reagent (a ca. 1:1 equilibrium mixture of the (s-*cis*- and s-*trans*-η^4-conjugated diene) metallocene diastereomers [7]) was added. An instantaneous reaction took place, and the 1:1 addition product (**4a**) between $Cp_2ZrCH_3^+$ and (butadiene)$ZrCp_2$ precipitated from the toluene solution as an oil.

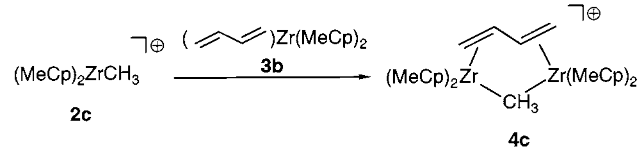
The product was isolated analytically pure (with 0.5 molar equivalents of toluene) as an amorphous solid after treatment with pentane. It is soluble in dichloromethane and this allowed for a detailed spectroscopic characterization.

Complex **4a** exhibits the $^1H/^{13}C$-NMR signals of two symmetry-equivalent pairs of diastereotopic cyclopentadienyl ligands (δ 5.88, 5.82/111.1, 109.0 ppm in d_2-dichloromethane). There is a single methyl group ($^1H/^{13}C$-NMR: δ 0.52/14.9 ppm) that is probably bridging between the two zirconium centers (the respective $CH_3[B]^-$ signals are observed at δ 0.84 (^1H) and δ 9.5 ppm (^{13}C)). The ^{13}C-NMR resonances of the μ-butadiene ligand are found at δ 113.0 (–CH=) and 44.3 (=CH_2, $^1J_{CH} = 148$ Hz) ppm. The corresponding ^1H-NMR butadiene resonances are observed at δ 3.41, 2.62 (=CH_2) and 3.37 (–CH=) ppm. These data strongly suggest that the butadiene ligand is symmetrically bridging the two zirconium centers in **4a** (i.e. attaining a μ-η^2:η^2-bonding mode), and that the μ-butadiene ligand favors a (distorted) s-*trans*-conformation in the cationic dinuclear complex **4a** [11,12].

Treatment of dimethylzirconocene with *N*,*N*-dimethylanilinium tetrakis(pentafluorophenyl)borate gave $Cp_2ZrCH_3^+$ with $B(C_6F_5)_4^-$ anion. Its subsequent reaction with (butadiene)zirconocene again gave the dinuclear $[(\mu\text{-butadiene})(\mu\text{-}CH_3)(ZrCp_2)_2^+]$ cation (**4b**), only in this case with the $B(C_6F_5)_4^-$ counteranion.



Treatment of $(CH_3\text{–}C_5H_4)_2Zr(CH_3)_2$ (**1b**) with $B(C_6F_5)_3$, followed by (η^4-butadiene)$Zr(CH_3\text{–}C_5H_4)_2$ (**3b**) [7] gave the analogous complex **4c**. Again, pairwise diastereotopic cyclopentadienyl ligands are observed at the zirconium centers. Due to the methyl substituent at the Cp-ring systems this leads to the occurrence of a set of eight equal intensity MeCp-methine ^1H-NMR CH resonances as well as eight separated ^{13}C-NMR MeCp–CH signals. The $^1H/^{13}C$-NMR resonances of the μ-η^2:η^2-butadiene ligand in complex **4c** occur in the typical range at δ 3.32/110.2 (–CH=) and 3.25, 2.37/46.8 (=CH_2) ppm.



cations with $CH_3B(C_6F_5)_3^{\ominus}$ anion

We have carried out a few reactions with the $[(Cp_2Zr)_2(\mu\text{-butadiene})(\mu\text{-}CH_3)]^+$ cation system **4a** that indicate some application potential in organometallic synthesis. The methyl-bridged complex **4a** reacts rather rapidly with the added reagent (methyl)zirconocene chloride (**1c**). Thus, treatment of a suspension of **4a** in toluene with dissolved $Cp_2Zr(CH_3)Cl$ produced the corresponding dinuclear chloride-bridged cation system **4d** as a rather insoluble oil within minutes. The product **4d** was isolated and characterized. Here the nicely separated ^1H-NMR signals of the μ-η^2:η^2-butadiene ligand [δ 3.41, 2.51 (=CH_2), 3.23 (–CH=)] allowed for a determination of the major J_{HH} coupling constants by spectral simulation. A comparison of selected data is shown in Table 1. This spectral analysis has revealed that the $^3J_{2\text{-H},3\text{-H}}$ coupling constant ($J_{aa'}$ in Table 1) amounts to ca. 16 Hz which strongly indicates the presence of a transoid geometry of the μ-butadiene ligand, in addition to the characteristic ^1H and ^{13}C-NMR chemical

Table 1
A comparison of characteristic ^{1}H-NMR chemical shifts and J_{HH} coupling constants of free butadiene (**6**) and the butadiene complexes s-*trans*-**3a**, **4d**, and s-*cis*-**5**[a]

δ/J_{HH} [a]	**4d**	s-*trans*-**3a**	**6**	s-*cis*-**5**[b]
δ(a)	3.23	2.85	6.26	4.31
δ(b)	3.41	3.18	5.05	2.60
δ(c)	2.51	1.16	5.16	0.37
$^3J_{aa'}$	16.4	15.9	10.4	7.9
$^3J_{ab}$	6.7	7.1	10.2	9.4
$^3J_{ac}$	12.0	16.6	17.1	11.1
$^2J_{bc}$	−4.5	−3.9	1.7	−4.1

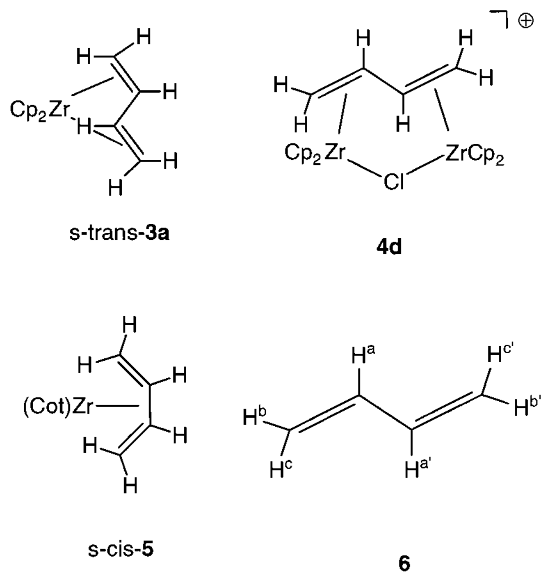
[a] See Scheme 1 for the structure of the compounds and the hydrogen atom notation at the C_4H_6 moieties.

[b] Literature values from Benn and Schroth [13].

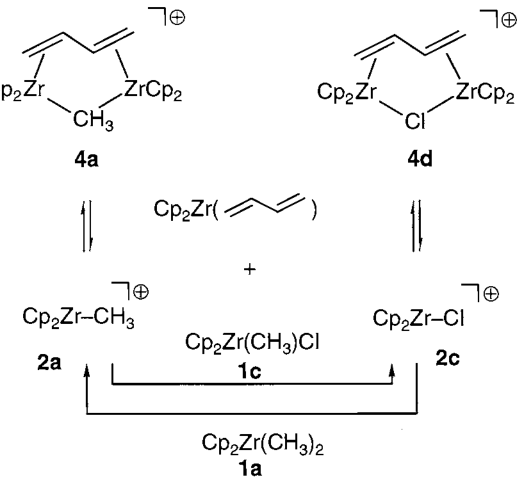
shifts of the butadiene ligand and the rather large $^1J_{CH}$ coupling constants at the butadiene =CH_2 terminus (Scheme 1).

A detailed mechanistic description of the **4a**→**4d** transformation must await further experimental evidence. But it is probably warranted to assume that this very facile exchange of the $Cp_2ZrCH_3^+$ moiety for a Cp_2ZrCl^+ unit in the systems **4** might indicate a kinetically favorable reversibility of the (butadiene)zirconocene/Cp_2ZrX^+-adduct formation. It must then be assumed that an additional equilibration takes place at the $Cp_2Zr–X^+$ cation stage from which the most electrophilic metallocene cation, namely here the $Cp_2Zr–Cl^+$ cation, is then preferentially trapped by the (butadiene)$ZrCp_2$ reagent present in the solution (see Scheme 2).

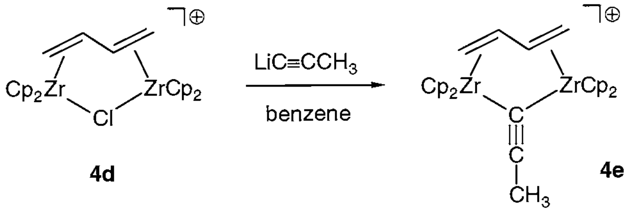
The chloride-bridged dinuclear cation can be used as a starting material for the preparation of the (butadiene)zirconocene adducts of other zirconocene-hydrocarbyl cations that are not easily accessible as such. A typical example is the very reactive $Cp_2Zr–C{\equiv}C–CH_3^+$ system (**2d**) [14]. Treatment of **4d** with one equivalent of propynyllithium gave the μ-acetylide bridged cation **4e**, that was isolated in ca. 60% yield (for its characterization see Section 3).



Scheme 1.



Scheme 2.



cations with $CH_3B(C_6F_5)_3^{\ominus}$ anion

This study has shown that the (butadiene)zirconocene reagent can very effectively be used to trap reactive Group 4 metallocene cations, such as $Cp_2ZrCH_3^+$ or Cp_2ZrCl^+. Such addition reactions lead to the formation of interesting novel dinuclear Group 4 metallocene cation complexes. It may eventually turn out that the (butadiene)$ZrCp_2$ moiety could be utilized as an organometallic protective group that stabilizes some Cp_2ZrX^+ systems, which may be tedious to handle as such, and may even allow some chemical transformations to be carried out with the protected Cp_2ZrX^+ complexes that are difficult to be performed with the sometimes very reactive mono-nuclear cations themselves [14]. For a synthetic use of these adducts it would, of course, be necessary to develop procedures that allow a clean liberation of the active Cp_2ZrX^+ species by deprotective cleavage of (butadiene)$ZrCp_2$ from the dimetallic complex systems. We are trying to develop such deprotection procedures that would make the reversible addition of the (butadiene)zirconocene reagent a useful tool in selective organometallic synthesis.

3. Experimental section

All reactions were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glovebox. Solvents (including deuterated solvents used for NMR measurements) were dried and distilled under argon prior to use. The following instruments were used for spectroscopic and physical characterization of the compounds: Bruker AC 200 P (^{1}H, 200 MHz; ^{13}C, 50 MHz), Bruker AM 360 (^{1}H, 360 MHz, ^{13}C, 90 MHz) and Varian Unity Plus (^{1}H, 600 MHz; ^{13}C, 150 MHz; ^{19}F, 564 MHz; ^{11}B, 192 MHz) FT–NMR spectrometer; in addition to the usual 1D experiments, the new compounds **4c**, **4d** and **4e** were also characterized by the following 2D-NMR experiments: GHSQC (gradient pulsed heteronuclear single quantum coherence) and GCOSY (gradient pulsed correlated spectroscopy); Nicolet 5DXC FT-IR spectrometer; elemental analyses: Foss Heraeus CHN-Rapid; melting points were determined by differential scanning calorimetry DSC 2010, Texas Instruments.

3.1. $[Cp_2Zr(\mu\text{-}\eta^2{:}\eta^2\text{-butadiene})(\mu\text{-}GH_3)Zr\text{-}Cp_2^+][B(C_6F_5)_3CH_3^-]$ **4a**

A mixture of dimethylzirconocene (**1a**) (50 mg, 0.20 mmol) and $B(C_6F_5)_3$ (100 mg, 0.20 mmol) was dissolved in 10 ml of toluene at room temperature to generate the cationic species **2a**. After the mixture was stirred for 5 min, a solution of (butadiene)zirconocene (**3a**) (54 mg, 0.20 mmol) in 5 ml of toluene was added. The reaction mixture was then stirred for 10 min at room temperature. During this time the product precipitated from the solution as a red oil. The solvent was decanted and the oily residue was washed with 20 ml of pentane and dried in vacuo for 3 h to give 0.10 g (49%) of **4a** as a red amorphous solid, m.p. 143°C (dec). ^{1}H-NMR (599.9 MHz, 278 K, dichloromethane-d_2): $\delta = 5.88, 5.82$ (s, each 10H, Cp), 3.41, 2.62 (m, each 2H, CH_2), 3.37 (m, 2H, CH), 0.84 (br, 3H, $CH_3{-}B(C_6F_5)_3^-$), 0.52 (br, 3H, μ-CH_3) ppm. ^{13}C-NMR (150.6 MHz, 253 K, dichloromethane-d_2): $\delta = 111.1$, 109.0 (Cp), 113.0 (*C*H), 44.3 (*C*H$_2$), 14.9 (μ-*C*H$_3$), 9.5 (br, *C*H$_3$–$B(C_6F_5)_3^-$); $MeB(C_6F_5)_3^-$: 148.6 (d, *o*-$B(C_6F_5)_3$, $^1J_{CF} = 244$ Hz), 137.9 (d, *p*-$B(C_6F_5)_3$, $^1J_{CF} = 243$ Hz), 136.5 (d, *m*-$B(C_6F_5)_3$, $^1J_{CF} = 245$ Hz), 128.7 (s, *i*-$B(C_6F_5)_3$) ppm. ^{13}C-NMR (90.6 MHz, 300 K, dichloromethane-d_2): $\delta = 111.1$, 109.0 (each d, Cp–*C*), 44.3 (t, *C*H$_2$, $^1J_{CH} = 148$ Hz), 9.5 (br, *C*H$_3$–$B(C_6F_5)_3^-$); $MeB(C_6F_5)_3^-$: 148.9 (d, *o*-$B(C_6F_5)_3$, $^1J_{CF} = 244$ Hz), 137.4 (d, *p*-$B(C_6F_5)_3$, $^1J_{CF} = 243$ Hz), 137.1 (d, *m*-$B(C_6F_5)_3$, $^1J_{CF} = 245$ Hz), 129.5 (s, *i*-$B(C_6F_5)_3$) ppm. The bridging CH_3-group and the CH of the butadiene unit were not observed under these conditions. IR (KBr): $\tilde{\nu} = 3118, 2851, 2920, 2960, 1500, 1263, 1088, 1018, 806, 735\ cm^{-1}$. According to the ^{1}H-NMR spectrum the product contains half an equivalent of toluene: Anal. calc. for $C_{44}H_{32}BF_{15}Zr_2$ (1038.95)·0.5 C_7H_8: C, 52.61; H, 3.30; found: C, 52.06; H, 3.27.

3.2. $[Cp_2Zr(\mu\text{-}\eta^2{:}\eta^2\text{-butadiene})(\mu\text{-}CH_3)Zr\text{-}Cp_2^+][B(C_6F_5)_4^-]$ **4b**

Dimethylzirconocene (**1a**) (12.5 mg, 0.05 mmol) and $[HNMe_2Ph^+][(B(C_6F_5)_4^-]$ (40 mg, 0.05 mmol) were dissolved in 0.5 ml of benzene-d_6 to generate the cationic species **2b**. After methane evolution had ceased, a solution of (butadiene)zirconocene (**3a**) (14 mg, 0.05 mmol) in 0.5 ml of benzene-d_6, was added. The product precipitated from the solution as a red oil. The benzene was decanted and the oily residue was dissolved in dichloromethane-d_2. ^{1}H-NMR (200.1 MHz, 300 K, dichloromethane-d_2): $\delta = 5.89, 5.83$ (each s, each 10H, Cp), 3.41, 2.61 (each m, each 2H, CH_2), 3.41 (m, 2H, CH), 0.52 (br, 3H, CH_3) ppm. ^{13}C-NMR (90.6 MHz, 300 K, dichloromethane-d_2): $\delta = 111.1$, 109.2 (each d, Cp), 44.5 (dd, *C*H$_2$, $^1J_{CH} = 150$ Hz and 144 Hz); $B(C_6F_5)_4^-$: 148.9 (d, *o*-$B(C_6F_5)_4$, $^1J_{CF} = 242$ Hz), 138.9 (d, *p*-$B(C_6F_5)_4$, $^1J_{CF} = 245$ Hz), 137.0 (d, *m*-$B(C_6F_5)_4$, $^1J_{CF} = 246$ Hz), 129.5 (s, *i*-$B(C_6F_5)_4$) ppm. The bridging CH_3-group and the CH of the butadiene unit were not observed.

3.3. $[(MeCp)_2Zr(\mu\text{-}\eta^2{:}\eta^2\text{-butadiene})(\mu\text{-}CH_3)Zr(Cp\text{-}Me)_2^+][B(C_6F_5)_3CH_3^-]$ **4c**

A mixture of bis(methylcyclopentadienyl)zirconiumdimethyl (150 mg, 0.54 mmol) and $B(C_6F_5)_3$ (280 mg, 0.54 mmol) were dissolved in 10 ml of benzene at room temperature to generate the cationic species **2c**. After the mixture was stirred for 5 min, a solution of (butadiene)bis(methylcyclopentadienyl)zirconium (**3b**) (170 mg, 0.54 mmol) in 5 ml of benzene was added. The reaction mixture was then stirred for 20 min at ambient temperature. During this time the product precipitated from the solution as a red oil. The solvent was decanted and the oily residue was washed with 20 ml of pentane and dried in vacuo for 3 h to give 210 mg (35%) of **4c** as a red amorphous solid, mp 183°C (dec). ^{1}H-NMR (599.9 MHz, 213 K, dichloromethane-d_2): $\delta =$ 5.73, 5.68, 5.62, 5.58, 5.56, 5.53, 5.51, 5.17 (each m, each 2H, $C_5H_4^-$), 3.32 (m, 2H, CH), 3.25, 2.37 (m, 4H, CH_2), 2.31, 2.45 (each s, each 3H, Cp–CH_3), 2.43 (s, 6H, Cp–CH_3), 0.84 (br, 3H, $CH_3{-}B(C_6F_5)_3^-$), 0.73 (br, 3H, μ-CH_3) ppm. ^{13}C-NMR (150.6 MHz, 213 K, dichloromethane-d_2): $\delta = 114.0$, 111.7, 111.0, 109.8, 109.3, 109.2, 106.9, 105.8 ($C_5H_4^-$), Cp–*C*), 110.2 (*C*H), 46.8 (*C*H$_2$), 15.0–14.7 (Cp–*C*H$_3$), 14.5 (μ-*C*H$_3$), 9.9 (br, *C*H$_3$–$B(C_6F_5)_3^-$); $MeB(C_6F_5)_3^-$: 149.0 (d, *o*-$B(C_6F_5)_3$, $^1J_{CF} = 238$ Hz), 137.6 (d, *p*-$B(C_6F_5)_3$, $^1J_{CF} = 242$ Hz), 136.1 (d, *m*-$B(C_6F_5)_3$, $^1J_{CF} = 241$ Hz) ppm. *i*-$B(C_6F_5)_3$ was not observed. ^{13}C-NMR (90.6 MHz, 300 K, dichloromethane-d_2): $\delta = 114.8$–107.1 (m, $C_5H_4^-$), 48.9 (dd, CH_2, $^1J_{CH} = 145$ Hz and 142 Hz), 9.7 (br, CH_3–B(C_6F_5)$_3^-$); MeB(C_6F_5)$_3^-$: 149.2 (d, *o*-B(C_6F_5)$_3$, $^1J_{CF} = 238$ Hz), 138.3 (d, *p*-B(C_6F_5)$_3$, $^1J_{CF} = 247$ Hz), 137.3 (d, *m*-B(C_6F_5)$_3$, $^1J_{CF} = 245$ Hz) ppm. The bridging CH_3-group and the B–C_i carbon were not observed under these conditions. The C_5H_4Me resonances overlap with the signal of the CH-unit of the butadiene unit which was therefore not located. GHSQC (599.9 MHz, 213 K, dichloromethane-d_2): $\delta = 114.0/5.56$, 111.0/5.68, 111.7/5.51, 109.8/5.58, 109.3/5.73, 109.2/5.62, 106.9/5.17, 105.8/5.53 ($C_5H_4^-$), 110.2/3.32 (CH), 46.8/3.25, 2.37 (CH_2), 15.0–14.7/2.31, 2.45, 2.43 (Cp–CH_3), 44.5/0.73 (CH_3), 9.9/0.84 (CH_3–B(C_6F_5)$_3^-$) ppm. GCOSY (599.9 MHz, 213 K, dichloromethane-d_2): $\delta = 3.32$ (CH)/3.25, 2.37 (CH_2) ppm. IR (KBr): $\tilde{\nu} = 3112$, 2961, 2931, 2868, 1641, 1511, 1457, 1380, 1265, 1087, 951, 803, 746, 661 cm^{-1}. Anal. calc. for $C_{43}H_{29}BF_{15}Zr_2$ (1023.2): C, 52.65; H, 3.68. found: C, 51.32; H, 3.61.

3.4. [$Cp_2Zr(\mu$-η^2:η^2-butadiene)(μ-Cl)Zr-Cp_2^+][B(C_6F_5)$_3$$CH_3^-$] **4d**

A mixture of dimethylzirconocene (**1a**) (50 mg, 0.20 mmol) and B(C_6F_5)$_3$ (100 mg, 0.20 mmol) was dissolved in 10 ml of toluene at room temperature to generate the cationic species **2a**. After the mixture was stirred for 5 min a solution of (butadiene)zirconocene (**3a**) (54 mg, 0.20 mmol) in 5 ml of toluene was added. The reaction mixture was then stirred for 10 min at room temperature. To this suspension was added (methyl)zirconocenechloride (**1c**) (54 mg, 0.2 mmol) in 5 ml of toluene and the mixture was stirred for 10 min at ambient temperature. The product was isolated analogously as described above to give 120 mg (60%) of **4d** as a dark red powder, mp 164°C (dec). ^{1}H-NMR (599.9 MHz, 278 K, dichloromethane-d_2): $\delta = 5.86$, 5.78 (each s, each 10H, Cp), 3.41, 2.51 (m, 4H, CH_2), 3.23 (m, 2H, CH), 0.46 (br, 3H, CH_3–B(C_6F_5)$_3^-$) ppm. ^{13}C-NMR (150.6 MHz, 253 K, dichloromethane-d_2): $\delta = 110.0$, 109.8 (Cp), 109.0 (CH), 44.3 (CH_2), 10.5 (br, CH_3–B(C_6F_5)$_3^-$); MeB(C_6F_5)$_3^-$: 148.4 (d, *o*-B(C_6F_5)$_3$, $^1J_{CF} = 230$ Hz), 137.8 (d, *p*-B(C_6F_5)$_3$, $^1J_{CF} = 245$ Hz), 136.3 (d, *m*-B(C_6F_5)$_3$, $^1J_{CF} = 240$ Hz) ppm. B–C_i carbon not observed. ^{13}C-NMR (90.6 MHz, 300 K, dichloromethane-d_2): $\delta = 110.1$, 109.9 (Cp), 45.1 (dd, CH_2, $^1J_{CH} = 153$ Hz and 145 Hz), 10.6 (br, CH_3–B(C_6F_5)$_3^-$); MeB(C_6F_5)$_3^-$: 148.2(d, *o*-B(C_6F_5)$_3$, $^1J_{CF} =$ 237 Hz), 137.4 (d, *p*-B(C_6F_5)$_3$, $^1J_{CF} = 243$ Hz), 137.1 (d, *m*-B(C_6F_5)$_3$, $^1J_{CF} = 245$ Hz), 129.5 (s, *i*-B(C_6F_5)$_3$) ppm. The bridging CH_3-group and the CH-unit were not observed under these conditions. GHSQC (599.9 MHz, 258 K, dichloromethane-d_2): $\delta = 110.0/5.86$ (Cp), 109.8/5.78 (Cp), 44.3/3.41, 2.51 (CH_2), 109.0/3.23 (CH), 10.5/0.46 (CH_3–B(C_6F_5)$_3^-$) ppm. IR (KBr): $\tilde{\nu} = 3119$, 2849, 2920, 2962, 1510, 1262, 1088, 1017, 806, 736 cm^{-1}. According to the ^{1}H-NMR spectrum the product contains half an equivalent of toluene: Anal. calc. for $C_{43}H_{29}BClF_{15}Zr_2$ (1059.37)·0.5 C_7H_8: C, 50.55; H, 2.96; found: C, 50.76; H, 3.38.

3.5. [$Cp_2Zr(\mu$-η^2:η^2-butadiene)(μ-C≡C–CH_3)Zr-Cp_2^+][B(C_6F_5)$_3$$CH_3^-$] **4e**

A mixture of dimethylzirconocene (**1a**) (50 mg, 0.20 mmol) and B(C_6F_5)$_3$ (100 mg, 0.20 mmol) was dissolved in 10 ml of benzene at room temperature to generate the cationic species **2a**. After the mixture was stirred for 5 min a solution of (butadiene)zirconocene (**3a**) (54 mg, 0.20 mmol) in 5 ml of benzene was added. The reaction mixture was then stirred for 10 min at room temperature. To this suspension was added $Cp_2Zr(CH_3)Cl$ (**1c**) (54 mg, 0.20 mmol) in 5 ml of benzene and stirred for 10 min at ambient temperature. After this time a suspension of propynyl lithium (12 mg, 0.26 mmol) in 5 ml of benzene was added. The resulting oily suspension was stirred for 2h. The solvent was then removed in vacuo and the oily residue was dissolved in 30 ml of dichloromethane. Lithium chloride was removed by filtration and the filtrate was evaporated to dryness. The residue was washed with 20 ml of pentane, and dried in vacuo for 3 h to give 130 mg (62%) of **4e** as a red amorphous solid, mp 187°C (dec). ^{1}H-NMR (599.9 MHz, 300 K, dichloromethane-d_2): $\delta = 5.55$, 5.44 (each s, each 10H, Cp), 3.95, 2.03 (each m, each 2H, CH_2), 2.91 (s, 3H, ≡C–CH_3), 1.57 (m, 2H, CH), 0.51 (br, 3H, CH_3–B(C_6F_5)$_3^-$) ppm. ^{13}C-NMR (150.6 MHz, 253 K, dichloromethane-d_2): $\delta = 106.5$, 106.2 (Cp), 92.2 (CH), 38.9 (CH_2), 13.0 (≡C–CH_3), 9.9 (br, CH_3–B(C_6F_5)$_3^-$); MeB(C_6F_5)$_3^-$: 148.0 (d, *o*-B(C_6F_5)$_3$, $^1J_{CF} = 252$ Hz), 137.7 (d, *p*-B(C_6F_5)$_3$, $^1J_{CF} = 246$ Hz), 136.2 (d, *m*-B(C_6F_5)$_3$, $^1J_{CF} = 233$ Hz) ppm. The B–C_i carbon and the carbon atoms of the alkynyl unit were not observed. GCOSY (599.9 MHz, 300 K, dichloromethane-d_2): $\delta =$ 3.95, 2.03 (CH_2)/1.57 (CH) ppm. GHSQC (599.9 MHz, 243 K, dichloromethane-d_2): $\delta = 106.5/5.55$ (Cp), 106.2/5.44 (Cp), 92.2/1.50 (CH), 38.9/3.95, 1.91 (CH_2), 13.0/2.91 (≡C–CH_3), 9.9/0.51 (CH_3–B(C_6F_5)$_3^-$) ppm. IR (KBr): $\tilde{\nu} = 3124$, 2964, 2913, 2848, 1640, 1510, 1458, 1266, 1087, 951, 808, 758 cm^{-1}. According to the ^{1}H-NMR spectrum the product contains half an equivalent of benzene: Anal. calc. for $C_{46}H_{32}BF_{15}Zr_2$ (1062.98)·0.5 C_6H_6: C, 53.40; H, 3.20; found: C, 54.73; H, 3.55.

Acknowledgements

Financial support from the Fonds der Chemischen Industrie, the Ministerium für Wissenschaft und Forschung des Landes Nordrhein–Westfalen, and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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