Notes

Structural Characterization of an (*s-trans*-η^4-Butadiene) Group 4 *ansa*-Metallocene Complex

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Summary: Treatment of the ansa-metallocene dichloride rac-$Me_2Si(C_5H_3CH_3)ZrCl_2$ *(**1**) with "butadiene-magnesium" gave a 82:8:10 mixture of the respective (s-trans-*η^4*-butadiene)metallocenes **2a** and **2b** and the (s-cis-butadiene)*$Me_2Si(C_5H_3CH_3)_2Zr$ *isomer, **2c**. One of the (s-trans-diene)metallocene isomers was characterized by X-ray diffraction. The typical bonding parameters of the (s-trans-*η^4*-butadiene)Zr unit are Zr−C1 2.453(3), Zr−C2 2.352(3), Zr−C3 2.338(2), and Zr−C4 2.455(3) Å. The butadiene C−C bond lengths are within a narrow range between 1.402(5) (C1−C2), 1.393(5) (C2−C3), and 1.364(6) Å (C3−C4). The C1−C2−C3−C4 torsional angle amounts to 124.3(4)°. These values are to be regarded as typical for (s-trans-*η^4*-butadiene) group 4 metallocene complexes.*

Introduction

(*s-trans*-η^4-Butadiene)zirconocene was the first example of a stable complex that had both olefinic units in a transoid conjugated diene conformation coordinated to the same transition metal center.[1] Since then such complexes have become more common.[2] They have evolved from stereochemical curiosities to valuable reagents in organic and organometallic synthesis[34] and in catalysis.[4] The structural characterization of their (*s-cis*-diene)metallocene isomers has never been problematic. A great number of very good and reliable X-ray crystal structure analyses has been reported in the literature over the years.[5] In contrast the number of high-quality (*s-trans*-η^4-butadiene)metal complex crystal structures has remained rather small, especially of the group 4 and 5 metals.[6] In a number of cases the detailed structural description of the available examples was seriously hampered by disordering effects inside the butadiene part of the molecule.[1,2,7] This may in several cases have been caused by enantiomeric superposition of the chiral molecular entities of the (*s-trans*-C_4H_6)-metallocene complexes in the crystal. A solution of this problem could then potentially be achieved by combining the chiral (*s-trans*-η^4-butadiene) subunit with a chiral metallocene backbone, thereby making the two possible (*s-trans*-η^4-butadiene)-coordination modes at the metallocene diastereomeric and thus readily physically separable. We have achieved this by using a chiral dimethylsilylene-bridged *ansa*-metallocene framework. A disorder-free (*s-trans*-η^4-butadiene)metallocene structure was thus characterized by X-ray crystal structure analysis, which may now serve as a suitable structural reference for this class of compounds.

Results and Discussion

We have selected the chiral C_2-symmetric *rac*-metallocene dichloride **1** as the starting material of our study.[8] The butadiene complexes were prepared by treatment with the butadiene-dianion equivalent "butadiene-magnesium".[1a] The a priori stereochemical product analysis reveals that the bent metallocene framework of the complexes **2** (and, of course, also of the *rac*-*ansa*-metallocene dichloride starting material **1**) contains a chiral axis (C_2-symmetry) that in the idealized framework geometry passes through both the Si and the Zr metal atom. This symmetry operation just leads to a

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† X-ray crystal structure analysis.

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[5] Reviews: Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1. Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120. A compilation of references on structurally characterized (*s-cis*-conjugated diene) group 4 and 5 metal structures is provided with the Supporting Information.

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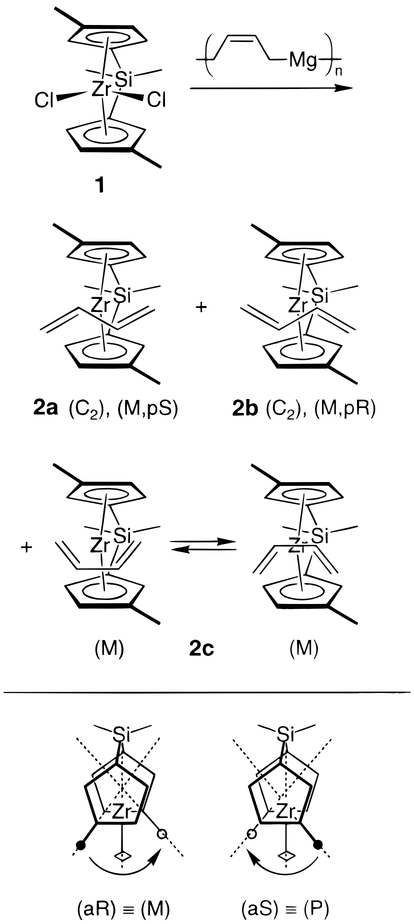
Scheme 1



positional exchange of the attached η^5-$C_5H_3CH_3$ ligands. The two enantiomers of the framework subunit can be assigned the stereochemical descriptors (aR) (i.e., "axially chiral R") or (aS). By convention these are identical with the descriptors (M) and (P), respectively,[9] if one options to describe the metallocene frameworks as helically chiral substructures. The used designators are depicted again at the bottom of Scheme 1 for clarity.

Attachment of the *s-trans*-η^4-butadiene ligand to the axially chiral metallocene framework introduces an additional chirality element, of local C_2-symmetry, into the molecule. Thus it is expected that two diastereoisomeric (*s-trans*-η^4-C_4H_6)$Me_2Si(C_5H_3CH_3)_2Zr$ complexes are formed. In the complex the attachment of the *s-trans*-butadiene moiety is to be described by the planar-chirality descriptors (pR) and (pS), respectively. The two diastereomers then are characterized by their relative configurations (M)(pS) (**2a**) and (M)(pR) (**2b**), respectively (of course, each will be formed as a racemate in this synthesis). Coordination of the *s-cis*-butadiene ligand of local C_s-symmetry does not introduce an additional chirality element. Consequently, only a single (*s-cis*-η^4-C_4H_6)$Me_2Si(C_5H_3CH_3)_2Zr$ diastereomer (**2c**) is expected to be formed.

This is actually observed. The reaction of the *ansa*-zirconocene dichloride $Me_2Si(C_5H_3CH_3)_2ZrCl_2$ (**1**) with butadiene-magnesium yielded a mixture of three (butadiene)metallocene diastereomers, namely, two (*s-trans*-η^4-C_4H_6)$Me_2Si(C_5H_3CH_3)_2Zr$ isomers (**2a** and **2b**) and a single corresponding (*s-cis*-η^4-C_4H_6)$Me_2Si(C_5H_3CH_3)_2Zr$ isomer (**2c**). These complexes were obtained in a 82:8:10 ratio in a combined yield of 76%.

The (*s-cis*-butadiene)(*ansa*-zirconocene) isomer **2c** shows temperature-dependent dynamic NMR spectra caused by the typical topomerization of the ZrC_4H_6 framework ("envelope-flip")[5,10] that is rapid on the NMR time scale at high temperature. At low temperature (253 K) it shows two equal intensity sets of ^1H (600 MHz) and ^{13}C (150 MHz) NMR signals of the symmetry-inequivalent $[Si]C_5H_3CH_3$ moieties and separated $Si(CH_3)_2$ resonances (^1H, 0.39, 0.35; ^{13}C, −4.5, −5.2) in addition to four butadiene ^{13}C NMR signals at δ 51.4, 50.6 (C1, C4), 112.2, 112.1 (C2, C3). From the coalescence of the $Si(CH_3)_2$ ^1H NMR resonances at 278 K and the pair of $[Si]C_5H_3CH_3$ ^1H NMR methyl signals at 288 K a Gibbs activation energy of $\Delta G^{\ddagger}_{top} = 13.6 \pm 0.3$ kcal mol^{-1} was obtained for the intramolecular automerization process of the (*s-cis*-diene)metallocene complex **2c**.

Each of the (*s-trans*-η^4-C_4H_6)metallocene isomers shows C_2-molecular symmetry in solution as expected. This leads to single $Si(CH_3)_2$ ^1H and ^{13}C NMR resonances for **2a** and **2b**, respectively [^1H: major isomer **2a** δ 0.30 and minor isomer **2b** δ 0.31]. The butadiene vinyl groups of each *s-trans*-isomer are symmetry-equivalent [^{13}C NMR: δ 99.0, 59.6 (**2a**); 97.4, 62.8 ppm (**2b**)].

Single crystals of one of the (*s-trans*-η^4-butadiene)$Me_2Si(C_5H_3CH_3)_2Zr$ isomers were obtained from a toluene solution of the mixture of the three diastereoisomers at −20 °C. The structure was solved with an *R*-value of <3% ($R_w{}^2 < 7\%$). There is a single (*s-trans*-diene)metallocene isomer present in the crystal (see Figure 1). It shows the typical chiral *ansa*-metallocene backbone. The 1,3-disubstituted η^5-cyclopentadienyl rings are connected by the $Si(CH_3)_2$ bridge (angle C11−Si−C21 95.9(1)°). The angle between the Cp-planes amounts to 127.7°. The methyl substituents at these Cp-ring systems are almost C_2-symmetrically arranged at the front side of the bent metallocene wedge and thus point to the "upper-left" and "lower-right" sectors.

The quality of the structure allowed a characterization of the typical bonding parameters of the (*s-trans*-η^4-butadiene)zirconium unit. The Zr−C1 (2.453(3) Å) and Zr−C4 (2.455(3) Å) bonds are markedly longer than the Zr−C2 (2.352(3) Å) and Zr−C3 (2.338(3) Å) bonds. The C1−C2 (1.402(5) Å), C2−C3 (1.393(5) Å), and C3−C4 (1.364(6) Å) bond lengths are in a very close range. The slight difference that is observed probably reflects the influence of the crystallographically asymmetric metallocene framework (that is chemically corresponding to a C_2-situation, however), at which the C_4H_6 ligand is oriented with the internal =CH− units directed toward the sectors of the Cp-methyl substituents (see Figure 1). The C1−C2−C3 angle amounts to 122.3(4)°; the C2−C3−C4 angle to 123.4(4)°. The C1−C2−C3−C4 torsional angle of the butadiene ligand is 124.3(4)°. Thus, the butadiene geometry in this typical (*s-trans*-η^4-butadiene)metallocene complex deviates substantially from that of the free ligand. The here observed structural data of the $(C_4H_6)Zr$ core can probably be

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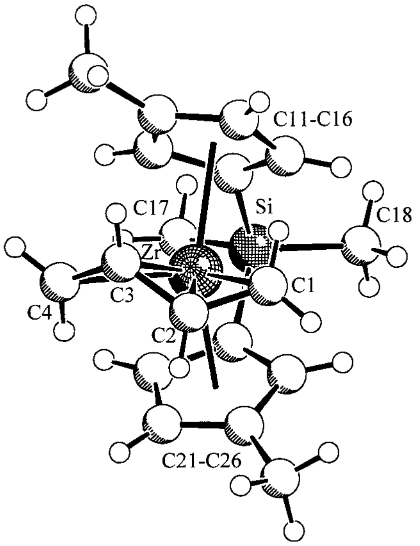

Figure 1. View of the (M)(pS) (*s-trans*-η^4-butadiene)$Me_2Si(C_5H_3CH_3)_2Zr$ diastereomer (only one enantiomer is depicted). Selected bond lengths (Å) and angles (deg): Zr−C1 2.453(3), Zr−C2 2.352(3), Zr−C3 2.338(3), Zr−C4 2.455(3), Zr−C_{Cp} 2.533, C1−C2 1.402(5), C2−C3 1.393(5), C3−C4 1.364(6), Si−C11 1.865(3), Si−C21 1.857(3), Si−C17 1.856(4), Si−C18 1.852(4); C2−C1−Zr 69.1(2), C3−C2−Zr 72.2(2), C1−C2−Zr 77.0(2), C4−C3−Zr 78.3(2), C2−C3−Zr 73.3(2), C3−C4−Zr 68.8(2), C1−C2−C3 122.3(4), C2−C3−C4 123.4(4), C11−Si−C21 95.9(1), C11−Si−C17 111.3(2), C11−Si−C18 111.8(2), C21−Si−C17 112.1(2), C21−Si−C18 111.1(2).

regarded as very characteristic for this general class of compounds.

Experimental Section

The reactions were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. The NMR spectra were measured on a Varian Unity Plus NMR spectrometer (^{1}H, 600 MHz; ^{13}C, 150 MHz). The starting material, *rac*-$Me_2Si(C_5H_3CH_3)_2ZrCl_2$ (**1**), was prepared according to a literature procedure.[8]

[Dimethylsilylene-bis(3-methylcyclopentadienyl)]-(butadiene)zirconium (2). To a mixture of *rac*-[dimethylsilylene-bis(3-methylcyclopentadienyl)]dichlorozirconium (**1**) (750 mg, 1.99 mmol) and "butadiene-magnesium" (532 mg, 2.39 mmol) was slowly added toluene (50 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for an additional 6 h at this temperature. The precipitate of magnesium chloride was filtered off. The red filtrate was concentrated under reduced pressure until the formation of a red solid could be observed, which was redissolved upon warming the slurry to 45 °C for 10 min. Cooling of the solution to −20 °C for 10 h result in the precipitation of butadiene complex **2** as red cubes, which were isolated by filtration, washed with pentane (5 mL), and dried in vacuo. Similar treatment of the filtrate yields an additional product fraction (total yield 544 mg, 76%, mp 141 °C). The two *s-trans*-butadiene forms and the *s-cis* isomer can be observed by NMR spectroscopy in a ratio of 82 (*s-trans* **A**):8 (*s-trans* **B**):10 (*s-cis*) at −20 °C. $C_{18}H_{24}SiZr$ (359.7): calcd C 60.11, H 6.73; found C 59.61, H 7.27. IR (KBr): $\tilde{\nu}$ = 3060 (w), 2955 (w), 2925 (w), 2899 (w), 1503 (w), 1440 (w), 1402 (w), 1254 (m), 1247 (s), 1160 (m), 1095 (s), 961 (m), 914 (m), 832 (s), 812 (vs), 805 (vs), 786 (s), 675 (s) cm^{-1}.

***s-trans* Isomer A (Major Isomer)**: ^{1}H NMR (599.9 MHz, toluene-d_8, 253 K) δ = 5.29, 5.09, 4.00 (m, each 2H, C_5H_3), 2.97 (m, 2H, butadiene−H_{syn}), 2.29 (m, 2H, H_{meso}), 1.33 (m, 2H, H_{anti}), 1.22 (s, 6H, $C_5H_3CH_3$), 0.30 (s, 6H, $Si(CH_3)_2$) ppm; ^{13}C NMR (150.8 MHz, toluene-d_8, 253 K) δ = 124.4 (C, cyclopentadienyl *C*−CH_3), 111.1 (CH, cyclopentadienyl−CH), 99.0 (CH, internal butadiene−CH), 96.7, 95.0 (each CH, cyclopentadienyl−CH), 88.5 (C, cyclopentadienyl *C*−Si), 59.6 (CH_2, terminal butadiene−CH_2), 13.7 (CH_3, $C_5H_3CH_3$), −5.4 (CH_3, $Si(CH_3)_2$) ppm.

***s-trans* Isomer B (Minor Isomer)**: ^{1}H NMR (599.9 MHz, toluene-d_8, 253 K) δ = 5.41, 5.13, 4.18 (m, each 2H, C_5H_3), 3.21 (m, 2H, butadiene−H_{syn}), 2.55 (m, 2H, H_{meso}), 1.05 (m, 2H, H_{anti}), 1.20 (s, 6H, $C_5H_3CH_3$), 0.31 (s, 6H, $Si(CH_3)_2$) ppm; ^{13}C NMR (150.8 MHz, toluene-d_8, 253 K) δ = 120.2 (C, cyclopentadienyl *C*−CH_3), 115.0, 97.8 (each CH, cyclopentadienyl−CH), 97.4 (CH, internal butadiene−CH), 95.2 (CH, cyclopentadienyl−CH), 89.5 (C, cyclopentadienyl *C*−Si), 62.8 (CH_2, terminal butadiene−CH_2), 14.9 (CH_3, $C_5H_3CH_3$), −5.3 (CH_3, $Si(CH_3)_2$) ppm.

***s-cis* Isomer (2c)**: ^{1}H NMR (599.9 MHz, toluene-d_8, 253 K) δ = 5.85, 5.57, 5.06, 4.95 (m, each 1H, C_5H_3), 4.81, 4.68 (each m, each 2H, each C_5H_3 and butadiene−H_{meso}), 3.35, 3.30 (m, each 1H, H_{syn}), 1.60, 1.46 (s, each 3H, $C_5H_3CH_3$), 0.39, 0.35 (s, each 3H, $Si(CH_3)_2$), −0.55, −1.11 (each m, each 1H, H_{anti}) ppm; ^{13}C NMR (150.8 MHz, toluene-d_8, 253 K) δ = 113.5 (CH, cyclopentadienyl−CH), 112.2, 112.1 (CH, internal butadiene−CH), 110.3, 106.3, 105.2, 102.3, 100.6 (CH, cyclopentadienyl−CH), 51.4, 50.6 (CH_2, terminal butadiene−CH_2), 15.3, 14.9 (CH_3, $C_5H_3CH_3$), −4.5, −5.2 (CH_3, $Si(CH_3)_2$) ppm. The resonances of cyclopentadienyl *C*−CH_3 and cyclopentadienyl *C*−Si were not detected.

Dynamic Behavior of 2c: ^{1}H NMR (599.9 MHz, toluene-d_8, 343 K) δ = 5.46, 5.32 (broad, each 2H, C_5H_3), 4.84 (broad m, 2H, C_5H_3), 4.73 (m, 2H, butadiene−H_{meso}), 1.53 (s, 6H, $C_5H_3CH_3$), 0.36 (s, 6H, $Si(CH_3)_2$) ppm. The signals of H_{syn} and H_{anti} were not detected at this temperature. Coalescence of the $Si(CH_3)_2$ protons is reached at ca. 278 K, $\Delta\nu$(253 K) = 21.62 Hz, $\Delta G^{\ddagger}$(278 K) = 13.7 kcal/mol; coalescence of the $C_5H_3CH_3$ protons is reached at ca. 288 K, $\Delta\nu$(253 K) = 82.24 Hz, $\Delta G^{\ddagger}$(288 K) = 13.5 kcal/mol.

X-ray Crystal Structure Analysis of 2. Crystals suitable for an X-ray structural analysis were obtained from a saturated solution of **2** in toluene at −20 °C; formula $C_{18}H_{24}SiZr$, M = 359.68, 0.40 × 0.30 × 0.20 mm, a = 7.284(1) Å, b = 15.168(1) Å, c = 15.259(1) Å, β = 94.56(1)°, V = 1680.5(3) Å^3, ρ_{calc} = 1.422 g cm^{-3}, μ = 7.15 cm^{-1}, empirical absorption correction via ψ scan data (0.763 ≤ T ≤ 0.870), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 223 K, $\omega/2\theta$ scans, 3669 reflections collected ($+h$, $+k$, $\pm l$), [(sin θ)/λ] = 0.62 Å^{-1}, 3400 independent (R_{int} = 0.013) and 2666 observed reflections [$I \geq 2\,\sigma(I)$], 185 refined parameters, R = 0.029, wR2 = 0.068, max. residual electron density 0.62 (−0.37) e Å^{-3}, hydrogens calculated and refined as riding atoms. Data set was collected with a Nonius MACH3 diffractometer, using a rotating anode generator FR591.[11]

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Supporting Information Available: Additional NMR data, a compilation of references on (*s-cis*-diene)metallocenes, details of the X-ray crystal structure analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Programs used: (data collection) *EXPRESS*; Nonius B. V., 1994. (data reduction) Fair, K. *MolEN*; Enraf Nonius B. V., 1990. (structure solution) Sheldrick, G. M. SHELXS-97. *Acta Crystallogr.* **1990**, *A46*, 467. (structure refinement) Sheldrick, G. M. *SHELXL-97*; Universität Göttingen, 1997. (graphics) Brandenburg, K. *DIAMOND*; Universität Bonn, 1996. Keller, E. *SCHAKAL*; Universität Freiburg, 1997.