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A binuclear zirconium fulvalene tetraallyl complex. The preparation and the molecular structure of $[\eta^5:\eta^5\text{-}C_{10}H_8][CpZr(\eta^1\text{-}CH_2CHCH_2)(\eta^3\text{-}CH_2CHCH_2)]_2$

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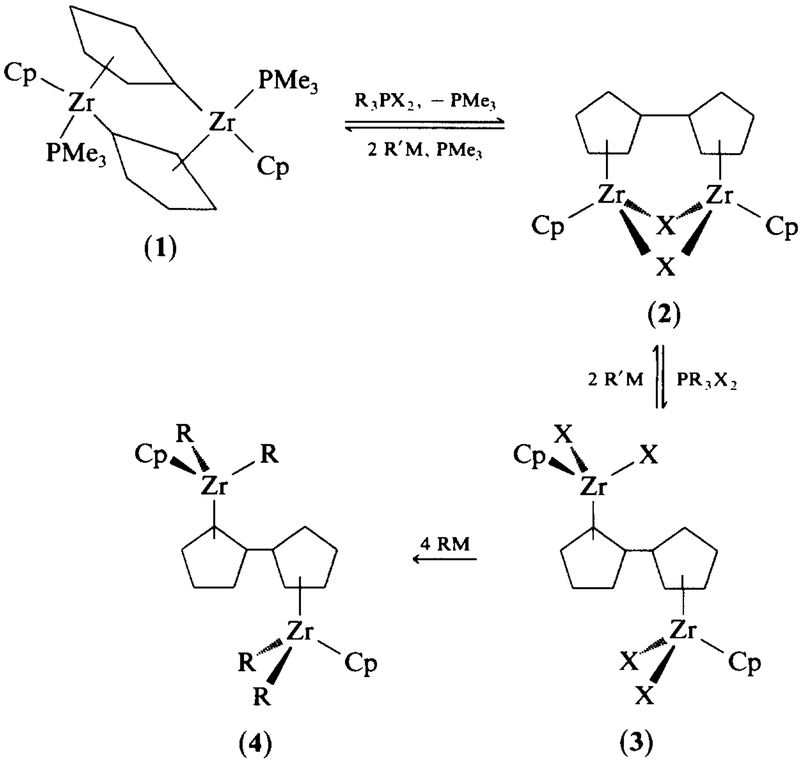
Abstract

Reaction of $[\eta^5:\eta^5\text{-}C_{10}H_8][CpZrX_2]_2$ (X = halide) with $(\eta^3\text{-}C_3H_5)MgCl$ in THF at room temperature allowed the isolation and characterization of *anti*-$[\eta^5:\eta^5\text{-}C_{10}H_8][CpZr(\eta^1\text{-}CH_2CHCH_2)(\eta^3\text{-}CH_2CHCH_2)]_2$ (**4b**) in good yield and crystalline form. Crystal data for **4b** are as follows: monoclinic, $P2_1/c$, $a = 7.990(1)$, $b = 18.522(3)$, $c = 18.272(1)$ Å, $\beta = 93.76(1)°$, $V = 2698.2(6)$ Å^3, $Z = 4$; least-squares refinement of 268 parameters and 2417 out of 3504 reflections converged to $R = 0.056$ and $R_w = 0.070$. NMR features suggest the occurrence in solution of rapid intramolecular rearrangements between two possible conformations of the allyl groups observed in the solid state structure.

Introduction

The close proximity between two transition metals in the same molecular frame is a desirable feature to verify the hypothesis that a cooperative interaction of two transition metals with the same substrate is able (i) to induce transformations otherwise not possible on a monometallic system, and (ii) to introduce a higher degree of stereoselectivity in the chemical reaction. Due to the enormous versatility of the zirconium-carbon bond in both catalysis [1] and metal promoted organic synthesis [2], we were especially interested in the preparation of dinuclear group 4 metal alkyl derivatives for reactivity studies.

The fulvalene ligand, formed by the reductive coupling of two cyclopentadienyl rings [3], is especially versatile for the preparation of homobimetallic systems [4]. Furthermore the almost free rotation around the C–C bond allows two possible conformations, *syn* and *anti*, with respect to the plane of fulvalene. When held in *syn* conformation, the two transition metals are forced to lie within a limited range of metal–metal distances (from 2.9 up to 4.0 Å) [5], which is an ideal feature to study the bimetallic activation of a substrate. Conversely, the *anti* conformation



Scheme 1. R = Me (**4a**), allyl (**4b**); R′ = CH_2Ph, phenyl, tolyl, ^{n}Bu, ^{t}Bu; X = Cl, Br, I; M = Li, MgCl.

makes bimetallic systems indistinguishable from mononuclear ones in terms of reactivity.

In this paper we describe the preparation and characterization of the dinuclear fulvalene zirconium allyl derivative *anti*-$[\eta^5:\eta^5\text{-}C_{10}H_8][CpZr(\eta^1\text{-}CH_2CHCH_2)(\eta^3\text{-}CH_2CHCH_2)]_2$ (**4b**) via alkylation reaction of *anti*-$[\eta^5:\eta^5\text{-}C_{10}H_8][CpZrX_2]_2$ (**3**) [6] (Scheme 1).

Experimental section

All the operations were performed under an inert atmosphere (N_2 or Ar) using standard Schlenk techniques, or in a nitrogen-filled dry-box (Vacuum-Atmospheres). $[\eta^5:\eta^5\text{-}C_{10}H_8][CpZrCl_2]_2$ was prepared following a published procedure [6]. Solvents were dried following standard procedures. Infrared spectra were recorded on a Perkin–Elmer 293 instrument, from Nujol mulls prepared in a dry-box. NMR spectra were recorded on a Varian Gemini 200 MHz spectrometer. Element analyses were carried out at the Microanalytical Department of the Chemistry Department of the State University of Groningen.

anti-$[\eta^5:\eta^5\text{-}C_{10}H_8][CpZr(\eta^1\text{-}CH_2CHCH_2)(\eta^3\text{-}CH_2CHCH_2)]_2$ (**4b**)

A solution of allylmagnesium chloride in THF (40 mL, 0.82 *M*, 32 mmol) was added, during 10 min at room temperature, to a slurry of $[\eta^5:\eta^5\text{-}C_{10}H_8][CpZrCl_2]_2$

(4.6 g, 7.8 mmol) in the same solvent (150 mL). The solid dissolved slowly to give a light orange solution. After evaporation of the solvent *in vacuo*, the residual solid was extracted with toluene. Light brown crystals of **4** were obtained after concentration and cooling at −30 °C (3.1 g, 5.1 mmol, 65% yield). Anal. Found: C, 63.30; H, 6.39; Zr, 30.38. for $C_{32}H_{38}Zr_2$ calcd.: C, 63.52; H, 6.33; Zr, 30.15%. ^{1}H-NMR (200 MHz, C_6D_6, 25 °C): δ 5.59 (quintet J(H–H) = 11.6 Hz, 4H, allyl); 5.31 (pseudo-t., 4H, fulvalene); 5.11 (pseudo-t., 4H, fulvalene); 5.08 (s., 10H, Cp); 2.89 (d., J(H–H) = 11.8 Hz, 16H, allyl). ^{13}C-NMR (75 MHz, C_6D_6, 25 °C): δ 137.3 (d. J(C–H) = 147.4 Hz, allyl); 114.5 (s., fulvalene); 105.9 (d., J(C–H) = 171.0 Hz, Cp); 103.9 (d., J(C–H) = 170.0 Hz, fulvalene); 103.8 (d., J(C–H) = 170.0 Hz, fulvalene); 65.2 (t., J(C–H) = 140.4 Hz, allyl).

X-Ray crystallography

A crystal of **4b** (a fragment cleaved from a larger crystal) was selected in a dry-box, sealed in a Lindemann capillary and mounted on a Enraf–Nonius CAD-4F diffractometer. The diffraction intensities were collected at 295 K with Mo-K_α radiation using the $\theta/2\theta$ scan mode with profile analysis [7]. Crystal and/or instrumental instability were monitored by the intensity of three reference reflections measured every 3 h of X-ray exposure time. The net intensities of the data collected in the range $1 < \theta < 22.4°$, were corrected for the scale variation, Lorentz and polarization effects, but not for absorption. The space group $P2_1/c$ was obtained by examination of systematic absences and the unit cell parameters were obtained by least-squares refinement of 25 reflections with 2θ angles in the range of 35–45 degrees. 2417 unique reflections out of 3504 unique satisfied the $I \geqslant 2.5\ \sigma(I)$ criterion of observability. The two zirconium atoms and the carbons atoms of one of the two crystallographically independent molecules were located by direct methods and refined anisotropically. Conversely the two cyclopentadienyl rings of the second molecule were found disordered over two positions (50% occupancy) and therefore were refined isotropically. The allyl groups were also found disordered on the second molecule. They were initially refined using a reasonable thermal parameter, while the occupancy was refined by using linking group. After a few cycles, the occupancy was fixed and the thermal parameters refined. Hydrogen atom were introduced at their calculated positions and therefore were not refined. The structure was refined by full matrix least squares to a final $R = 0.056$ ($R_w = 0.070$), for the significant reflections, maximum shift/error = 0.803. Pertinent numerical data on structure determination and refinement are given in Table 1. Final atomic coordinates are given in Table 2; relevant bond distances are given in Table 3. Extensive lists of values on molecular geometry and tables of observed and calculated structure factors are given as Supplementary material available. All calculations were carried out on the VAX computer with the program package NRCVAX Crystal Structure Package [8].

Results and discussion

The complex was prepared, following a standard procedure, by treating a slurry of $[\eta^5:\eta^5\text{-}C_{10}H_8][CpZrCl_2]_2$ in THF with an excess of $(\eta^3\text{-}C_3H_5)$MgCl at room temperature (Scheme 1). After filtration and evaporation, large crystals of **4b** were obtained in reasonable yield (65%) upon crystallization from toluene at −30 °C.

Table 1

Crystal data and structure refinement

Formula	$C_{32}H_{38}Zr_2$
Mol. wt.	605.09
Crystal system	monoclinic
Space group	$P2_1/c$
Z	4
a (Å)	7.990(1)
b (Å)	18.522(3)
c (Å)	18.272(1)
β	93.76(1)
V (Å^3)	2698.2(6)
D_{calcd} (g cm^{-3})	1.490
μ (absorp. coeff.) (mm^{-1})	0.78
$F(000)$	1239.64
radiation (Mo-K_α) (Å)	0.71073
T (K)	295
θ range, max. min. (deg)	1.00, 22.4
Total data	5028
Unique data	3504
Observed data	2417 $I \geqslant 2.5\sigma(I)$
Number of parameters	268
R_F, R_w, S	0.056, 0.070
shift/σ	0.803

Complex **4b** is thermally stable and no significant decomposition was observed when a toluene solution was heated for 24 h (100 ° C). Similar stability was observed for the methyl derivative *anti*-[η^5 : η^5-$C_{10}H_8$][$CpZrMe_2$]$_2$ (**4a**) having similar geometry [6].

Table 2

Fractional atomic coordinates and equivalent isotropic thermal parameters

Atom	x	y	z	B_{iso}
Zr1	0.05427(13)	0.51479(6)	0.33521(6)	3.68(5)
C11	0.2586(18)	0.4348(8)	0.4075(7)	4.7(7)
C12	0.1063(17)	0.4271(7)	0.4427(6)	3.7(6)
C13	0.0690(13)	0.4931(6)	0.4765(6)	2.4(5)
C14	0.1989(14)	0.5438(7)	0.4626(6)	3.2(2)
C15	0.3130(14)	0.5059(9)	0.4203(7)	4.6(7)
C11′	0.2734(16)	0.5023(8)	0.2448(6)	4.2(7)
C12′	0.1199(18)	0.4895(10)	0.2048(7)	5.4(8)
C13′	0.0328(17)	0.5555(10)	0.2025(7)	5.7(9)
C14′	0.1309(19)	0.6079(8)	0.2397(8)	5.0(7)
C15′	0.2794(16)	0.5738(8)	0.2666(7)	3.9(6)
C16	−0.0834(15)	0.6278(7)	0.3717(7)	3.8(6)
C17	−0.2067(16)	0.5937(9)	0.3274(8)	4.8(7)
C18	−0.2661(15)	0.5264(9)	0.3415(9)	5.4(8)
C19	−0.0830(17)	0.4024(8)	0.3001(9)	5.1(8)
C20	0.0288(19)	0.3404(9)	0.2887(11)	6.8(10)
C21A	0.049(4)	0.3003(18)	0.2428(17)	5.4(16)

Table 3

Selected bond distances (Å)

Zr1–C16	2.49(1)	Zr1–C17	2.54(1)
Zr1–C18	2.58(1)	Zr1–C19	2.45(1)
C16–C17	1.40(2)	C17–C18	1.31(2)
C19–C20	1.49(2)	C20–C21A	1.07(4)
C13–C13A	1.38(1)		

The molecular structure of **4b**, as determined by X-ray diffraction analysis, showed the unit cell composed by two crystallographically independent but chemically equivalent molecules, each lying on an inversion center. The molecular geometry of one of these is reported in Fig. 1 (Plot of the disordered molecule can be obtained, see Supplementary material available section). The molecule has the *anti* configuration previously observed in some other Zr^{IV} fulvalene derivatives [6]. The fulvalene moiety is almost perfectly planar [torsion angle C12–C13–C13a–C12a = 180.0(16)°]. Each of the two zirconium atoms is coordinated to fulvalene, one η^5-Cp ring and two allyl groups, in an overall pseudo-tetrahedral geometry. The non-equivalency of the two allyl groups can be described in terms of different modes of ligation to zirconium (η^3- versus η^1-). Conformational disorder over two positions (50% occupancy) has been observed for the cyclopentadienyl rings and the two allyl groups in one of the two independent molecules (see Supplementary material available section). The conformational disorder which affects the allyl

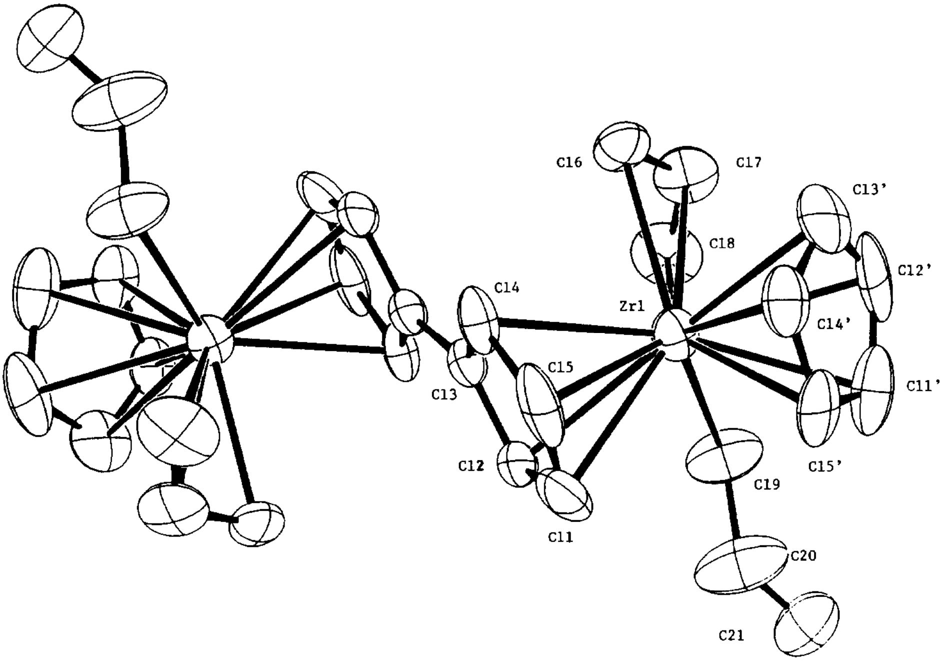


Fig. 1. ORTEP drawing of **4b** showing the labeling scheme with thermal ellipsoids drawn at the 50% probability level.

groups, has been modeled by splitting the occupancy (50%) of each allyl group over each of the two possible conformations (η^3- and η^1-) with respect to zirconium. The η^1-allyl group is quite regular [C19–C20 = 1.49(2) Å; C20–C21A = 1.07(3) Å] and has a Zr–C bond distance of 2.45(1) Å, which is considerably longer than that observed in the mononuclear $CpZr(allyl)_3$ [9]. The η^3-bonding mode of the second allyl group [C16–C17 = 1.40(2) Å, C17–C18 = 1.31(2) Å] is also quite regular, although the differences between the Zr–C distances [Zr1–C16 = 2.49(1) Å, Zr1–C17 = 2.54(1) Å, Zr1–C18 = 2.58(1) Å] are more considerable than in other allyl complexes [9].

The solid state IR spectrum (Nujol mull) showed the presence of only one resonance (1585 cm^{-1}) in the region 1600–1500 cm^{-1}, which may suggest the exclusive presence of η^1-allyl groups, the η^3-bonding mode of the second allyl group being then only an artifact of the solid state structure [9]. By way of contrast, the surprisingly simple NMR spectra are consistent with the presence in solution of symmetrically bonded η^3-allyl only [9]. No line broadening was observed at variable temperature in the range $-80/+90\,^\circ C$ for both the ^1H- and ^{13}C-NMR spectra. These results can be explained with the same type of conformational disorder observed in one of the two independent molecules, which suggest the presence in solution of a highly fluxional behavior between the two conformations (η^1- and η^3-), able to rapidly interconvert into each other. Furthermore, a fast intramolecular allyl exchange reaction between the two metal centers can also be expected, due to the easy rotation around the fulvalene C–C linkage, easily interconverting the *syn* and *anti* conformations [6]. We believe that the NMR data may be explained, rather than with the improbable existence in solution of 20 electron zirconium atoms with two η^3-allyl groups, by rapid exchange between several possible conformations of the two allyl groups, with an overall average geometry which closely resembles that of a η^3-allyl group.

Attempts to prepare different alkyl analogues in the usual reaction conditions (^nBu, CH_2Ph, phenyl, tolyl) failed and the resulting deeply colored solutions gave the characteristic NMR signals of $\eta^1:\eta^5\text{-}C_5H_4$ rings [10]. This suggests that reduction of the metal centers occurs in these cases, accompanied by cleavage of the fulvalene. Although precedented [6,11] this cleavage was quite unexpected in this case, due to the reasonable stability of the corresponding mononuclear alkyl biscyclopentadienyl derivatives [1a]. The general failure to obtain Zr^{IV} fulvalene tetra-alkyl derivative $[\eta^5:\eta^5\text{-}C_{10}H_8][CpZrR_2]_2$ was the result of instability of the intermediate $[\eta^5:\eta^5\text{-}C_{10}H_8][CpZrRX]_2$ towards reductive elimination and formation of the thermally robust Zr^{III} derivatives $[\eta^5:\eta^5\text{-}C_{10}H_8][CpZrX]_2$ (**2**) (X = Cl, Br, I, SR) [6]. These species were isolated in high yield and fully characterized when $[\eta^5:\eta^5\text{-}C_{10}H_8][CpZrX_2]_2$ was treated with only two equivalents of RLi (Scheme 1). The cleavage of fulvalene, obtained by further reaction of $[\eta^5:\eta^5\text{-}C_{10}H_8][CpZrX]_2$ with RLi, occurs due to the limited ability of bridging alkyl groups to stabilize the Zr–X–Zr–X frame. The additional stability provided by a questionable Zr–Zr bond would be expected to be considerably small, if any [4c,5c,6a].

These considerations prompted us to test the reactivity of the fulvalene tetraalkyl derivatives **4** with reagents containing acidic protons (H_2O, ROH, R_2NH, etc.) which could possibly stabilize the intermediate $[\eta^5:\eta^5\text{-}C_{10}H_8][CpZrRX]_2$ (X = $\frac{1}{2}$O, OR, NR_2) and might work as suitable starting materials for further alkylation reactions. While the reaction of **4a** with stoichiometric amounts of water restored the *syn* configuration of the two metal centers leading to *syn*-[η^5 : η^5-$C_{10}H_8$][$CpZr(CH_3)$]$_2$[μ-O] [6], the reaction with a number of alcohols gave only *anti*-[η^5 : η^5-$C_{10}H_8$][$CpZr(OR)_2$]$_2$ species. Conversely the reaction of **4b** with (−)-menthol allowed the isolation in crystalline form of *anti*-[η^5 : η^5-$C_{10}H_8$][CpZr(η^3-CH_2CHCH_2)(OMt)]$_2$ [Mt = (−)-menthyl] [12]. The use of this complex for the preparation of mixed alkyl species will be investigated in the near future.

Supplementary material available. ORTEP plot of the disordered independent molecule, listings of atomic positional and thermal parameters, anisotropic thermal parameters, complete bond distances and angles, and observed and calculated structure factors (22 pages) can be obtained from the authors.

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