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Structure of an oxazirconacyclohexadiene synthesized by thermolysis of difurylzirconocene

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Abstract

Thermolysis of bis(2-furyl)zirconocene **1** at 185°C gives 1,1-bis(η-cyclopentadienyl)-1-zircona-2-oxa-6-(2′-furyl)cyclohexa-3,5-diene **2** *via* a coupled σ,σ-exchange reaction. Complex **2** was characterized by X-ray diffraction and shown to be monomeric in the crystal and to have a non-planar twist-like oxametallacyclohexadiene ring conformation.

Introduction

Metallacyclopentadienes of the early transition metals can be readily prepared and so many differently-substituted examples are known [1]. However, the corresponding conjugated metallacyclohexadiene derivatives cannot be prepared in such a straightforward manner. Examples of metallacyclic six-membered ring systems containing sp^2-hybridized carbon atoms in the ring are rather rare. We have recently found a simple synthetic route to oxa- and thia-zirconacyclohexadienes that makes use of a thermally-induced migratory ring enlargement reaction. Thermolysis of a variety of $Cp_2Zr(R)(\sigma$-furyl) and –(σ-thienyl) derivatives proceeded by insertion of the Cp_2Zr-moiety into the chalcogene to carbon σ-bond of the adjacent organic five-membered σ-ligand ring system (to give the ring-enlarged chalcogenazirconacyclohexadiene) [2]; at the same time migration of the R group from zirconium to the α-carbon of the ring system took place and completed the overall coupled σ,σ-exchange reaction [3].

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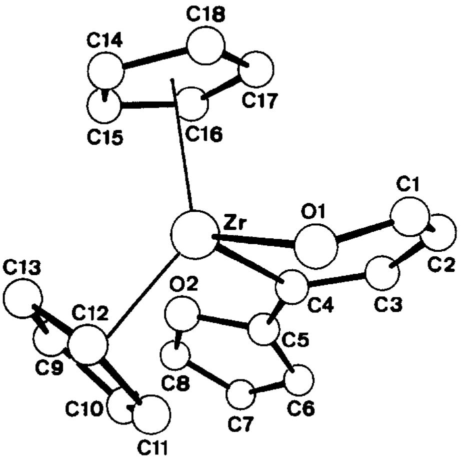
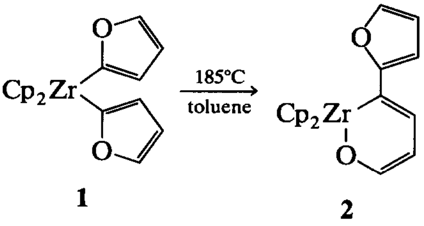


Fig. 1. A view of the molecular structure of 2.

A typical example is the thermolysis of difurylzirconocene **1**. The rearrangement takes place rapidly at 185°C to give the oxazirconacyclohexadiene **2** in a very clean reaction (*ca.* 90% yield of isolated product). The activation parameters for the $\mathbf{1} \rightarrow \mathbf{2}$ first order rearrangement were found to be $\Delta H^{\ddagger} = 30.9 \pm 2.0$ kcal mol^{-1} and $\Delta S^{\ddagger} = -9 \pm 5$ cal mol^{-1} K^{-1} [2b]. We have now obtained crystals of this unusual organometallic six-membered metallacyclic product suitable for X-ray diffraction, and determined its molecular structure in the solid state.



The crystal is made up of discrete molecules of complex **2**. The bis(η-cyclopentadienyl)zirconium bent metallocene unit is part of a six-membered oxametallacyclohexadiene moiety. The conjugated diene portion [C1 to C4] is slightly folded, the C1–C2–C3–C4 torsion angle being 15.4°. The Zr–O1 vector is clearly located away from the mean C1 to C4 plane. This results in an overall twist-like conformation of the oxazirconacyclohexadiene ring-system. Both heteroatoms are located outside the conjugated diene plane with the metal atom lying 0.49 Å above and the oxygen centre 0.28 Å below it.

The conjugated diene in the six-membered ring exhibits an alternating bond length sequence as expected [4], viz. 1.358(3) Å (C4–C3), 1.438(3) Å (C3–C2) and 1.338(4) Å (C2–C1). The C1–O1 σ-bond length is 1.336(3) Å. The metal–oxygen bond length is slightly more than 2 Å (Zr–O1: 2.017(2) Å). The adjacent zirconium to carbon bond is much longer at 2.273(2) Å, which is probably a normal value for a $Cp_2Zr{-}C(sp^2)$ σ-bond [5]. The bond lengths and the overall geometry of the oxazirconacyclohexadiene do not reveal any unusual metal–diene conjugative effects. The structural features of this six-membered ring system are quite different

Table 1

Selected distances and angles in **2**

Zr-O1	2.017(2)	Zr-C4	2.273(2)
O1-C1	1.336(3)	O2-C5	1.379(3)
O2-C8	1.352(4)	C1-C2	1.338(4)
C2-C3	1.438(3)	C3-C4	1.358(3)
C4-C5	1.448(3)	C5-C6	1.360(4)
C6-C7	1.408(4)	C7-C8	1.330(4)
C4-Zr-O1	88.3(1)	C1-O1-Zr	121.5(2)
C8-O2-C5	107.1(2)	C2-C1-O1	124.8(2)
C3-C2-C1	127.3(2)	C4-C3-C2	128.0(2)
C5-C4-C3	117.9(2)	C5-C4-Zr	127.0(2)
C3-C4-Zr	115.1(2)	C6-C5-C4	135.6(2)
C6-C5-O2	107.7(2)	C4-C5-O2	116.6(2)
C7-C6-C5	107.8(2)	C8-C7-C6	106.3(3)
C7-C8-O2	111.0(3)		

from those of the few transition metal-containing heteroaromatic systems that have become known recently [6]. Complex **2** behaves more like a heteroatom-containing organometallic analogue of a substituted 1,3-cyclohexadiene ring system.

The incorporation of the two heteroatoms leads to a slight distortion of the cyclohexadiene-like ring. The endocyclic bond angles at carbon atoms C1 to C3 are

Table 2

Atomic coordinates and equivalent isotropic thermal parameters (Å^2) for **2**

Atom	x	y	z	U_{eq} ^{a}
Zr	0.5402(1)	0.3575(1)	0.0662(1)	0.034
O1	0.5340(1)	0.2761(1)	0.0489(2)	0.046
O2	0.4072(1)	0.4463(1)	0.3024(2)	0.062
C1	0.4563(2)	0.2506(1)	0.0153(3)	0.048
C2	0.3749(2)	0.2651(1)	0.0715(3)	0.049
C3	0.3539(2)	0.3110(1)	0.1710(3)	0.042
C4	0.4062(1)	0.3551(1)	0.2010(3)	0.036
C5	0.3731(2)	0.3945(1)	0.3155(3)	0.039
C6	0.3151(2)	0.3938(1)	0.4424(3)	0.052
C7	0.3139(2)	0.4460(1)	0.5100(4)	0.061
C8	0.3696(3)	0.4760(1)	0.4214(4)	0.069
C9	0.6292(2)	0.4206(1)	0.2414(4)	0.071
C10	0.5980(2)	0.3807(1)	0.3444(3)	0.061
C11	0.6397(2)	0.3327(1)	0.3035(4)	0.066
C12	0.6971(2)	0.3424(2)	0.1741(5)	0.074
C13	0.6913(2)	0.3973(2)	0.1364(4)	0.078
C14	0.5845(2)	0.3982(1)	−0.1952(3)	0.059
C15	0.5297(2)	0.4367(1)	−0.1201(4)	0.055
C16	0.4421(2)	0.4161(1)	−0.1122(3)	0.055
C17	0.4422(2)	0.3650(1)	−0.1830(3)	0.062
C18	0.5301(3)	0.3543(1)	−0.2352(3)	0.067

^{a} $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$.

slightly larger than expected for sp^2-hybridized carbon at 124.8(2)° (O1–C1–C2), 127.3(2)° (C1–C2–C3), 128.0(2)° (C2–C3–C4), whereas the C3–C4–Zr angle (115.1(2)°) is slightly smaller. The C4–Zr–O1 angle is 88.3(1)° [7]. The Zr–O1–C1 angle is at 121.5(2)°, considerably larger than the carbon–oxygen–zirconium angle found in many five-membered oxazirconacyclic systems [8]. This may allow some oxygen to zirconium electron donation to take place in the σ-ligand plane and reduce the electron deficit at the early transition metal centre. This slight tendency for oxygen to zirconium backbonding in **2** may just provide the necessary extra electronic stabilization that makes this oxazirconacyclohexadiene stable as a monomer even in the solid state [9*] in contrast to many known oxazirconacyclopentanes, which are isolated almost exclusively as Zr–O bonded dimers [8].

It remains to be checked whether the attached 2-furyl substituent can stabilize the Zr-centre in complex **2**. The former σ-(2-furyl) ligand becomes connected to the diene carbon atom C4 at the six-membered ring in the **1** → **2** rearrangement reaction. The furyl ring system is planar. The carbon–carbon bond lengths are 1.360(4) Å (C5–C6), 1.408(4) Å (C6–C7), 1.330(4) Å (C7–C8), and the carbon oxygen bond lengths are 1.379(3) Å (C5–O2) and 1.352(4) Å (C8–O2). In order to accommodate the four carbon atoms and an oxygen in the planar five-membered ring system, the sp^2-carbon and oxygen angles are much reduced [observed: 107.7(2)° (O2–C5–C6), 107.8(2)° (C5–C6–C7), 106.3(3)° (C6–C7–C8), 111.0(3)° (C7–C8–O2), and 107.1(2)° (C8–O2–C5)]. All these bonding features are as usually observed for furyl ring systems [4].

The C1 to C4 and C5 to C8 conjugated C=C–C=C systems are not coplanar. They are rotated just enough [dihedral angle θ (C3–C4–C5–C6) = 24.9°] to allow for sufficient minimization of the unfavourable H–C3 *vs*. H–C6 interaction. This angle between the extended π-electron systems at C1–C2–C3–C4 and C5–C6–C7–C8 probably does not completely inhibit conjugation between these two ring systems.

The connecting linkage between the two conjugated diene portions (C4–C5: 1.448(3) Å) is the longest carbon–carbon σ-bond present in complex **2**. It should be noted that the planar furyl ring system is rotated around the C4–C5 bond in such a way that the furyl ring oxygen O2 becomes oriented towards the zirconium centre. In fact, both the zirconium atom inside the six-membered ring and O2 inside the five-membered ring become located at the same face relative to the C1 to C4 conjugated diene plane (*i.e.* O2 and Zr both lie above the C1–C2–C3–C4 plane when O1 is oriented below it). The Zr–C4–C5–O2 torsional angle is 24.4°. The Zr–C4 and C5–O vectors are in an *s-cis*-orientation at the C4–C5 linkage.

The O2–C5–C4 angle is 116.6(2)°. The corresponding angle at C4 is even larger, at 127.0(2)° (Zr–C4–C5). Therefore, the O2 ··· Zr separation is quite large at 3.540(2) Å. We conclude that the furyl oxygen is probably not close enough to the metal to indicate a significant electronic stabilization of the electron-deficient zirconium centre by internal coordination (*e.g.* similar to the well known η^2-acyl-, -iminoacyl-, -alkoxymethyl-, or -phosphinomethyl-ligand systems [10]). However, the furyl oxygen should shield the electrophilic zirconium centre effectively from nucleophilic attack from the lateral position in which it is located. We are currently

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* Reference number with asterisk indicates a note in the list of references.

investigating whether this special situation can be used for studying insertion reactions into the sterically unshielded zirconium to oxygen σ-bond of the six-membered metallacyclic ring system.

Experimental

1,1-Bis(η-cyclopentadienyl)-1-zircona-2-oxa-6-(2′-furyl)cyclohexa-3,5-diene **2** was prepared by thermally induced rearrangement of bis(2-furyl)zirconocene **1** as previously described [2b]. Crystals were obtained by crystallization of complex **2** from toluene.

X-ray crystal structure determination of 2

A suitable crystal (dimensions 0.35 × 0.42 × 0.14 mm) of **2** was mounted under argon in a glass capillary. Data ($\pm h$, $+k$, $+l$) were collected at 293 K on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å). Cell constants, obtained from a least-squares refinement with the setting angles of 25 centred reflections ($11.50° \le \theta \le 16.80°$), corresponded to an orthorhombic cell with cell dimensions a = 14.742(1) Å, b = 24.684(2) Å, c = 8.331(1) Å, V = 3031.6 $Å^3$; Z = 8, calculated density = 1.56 g cm^{-3}, $F(000)$ = 1440 e, and μ = 7.13 cm^{-1} (no absorption correction applied). Space group *Pccn* (No. 56). A total of 11725 reflections [ω–2θ scan technique, $(\sin\theta)/\lambda_{max}$ = 0.74 $Å^{-1}$] was collected, of which 5258 were unique (R_{av} = 0.03); 3551 observed reflections [$I > 2\sigma(I)$] were used for the structure solution (direct method, SHELX-86 and subsequent full-matrix least-squares refinement. All non-hydrogen atoms were refined anisotropically, all H atoms were placed in calculated positions and kept fixed in the final refinement; R = 0.037, R_w = 0.041 [$w = 1/\sigma^2 (F_o)$]; GOF = 1.40; final residual electron density = 0.33 e $Å^{-3}$. Final atomic parameters are listed in Table 2. Further details of the structural investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Germany, on quoting the depository number CSD-56218, the names of the authors, and the journal citation.

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