# Synthesis and Characterization of 2-[Di(cyclopentadienyl)zircona]-1-oxacyclopentanes. *X*-Ray Crystal Structure of $[(\eta\text{-}C_5H_5)_2\overline{ZrOCH_2CH_2CH}Me]_2$

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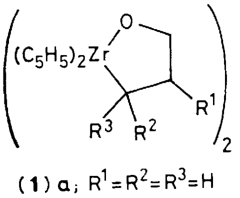
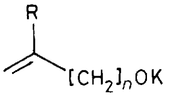
2-[Di(cyclopentadienyl)zircona]-1-oxacyclopentanes have been synthesized, isolated, and characterized by spectroscopic and *X*-ray analyses which show that they are dimeric with five co-ordinated bent metallocene structures; the mechanisms of their thermal decomposition have also been studied.

Metallacycle compounds are of increasing interest because of their importance as intermediates in many useful transition metal catalysed organic reactions. There are only a limited number of reports on the preparations and reactions of metallacycles which contain an oxygen atom in their rings.[1] We now report the synthesis and thermal reactions of the parent 2-[di(cyclopentadienyl)zircona]-1-oxacyclopentane (**1a**) and its derivatives.[2]

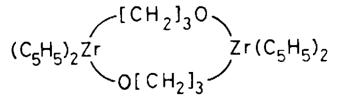
Treatment of $(\eta\text{-}C_5H_5)_2ZrHCl$ with the alkoxide (**2a**) in tetrahydrofuran at room temperature followed by recrystallization of the product from chloroform afforded (**1a**). Similar reaction of (**2b**) gave (**1b**), while (**2c**) gave only (**1c**). No six-membered metallacycles were isolated. The isolation yields of (**1a—c**) were 10—40%.[3] The compound (**1a**) was also prepared in 60% yield by the reaction of zirconocene dichloride with the Normant Grignard reagent[4] derived from 3-chloropropan-1-ol. The structures of (**1a—c**) were determined mainly from their spectral data [*e.g.*, for (**1a**), $^1H$ n.m.r. ($CDCl_3$) $\delta$ 1.03 (t, $J$ 6.2 Hz, $ZrCH_2$), 1.85 (m, $ZrCH_2CH_2$), 3.52 (t, $J$ 5.5 Hz, $OCH_2$), and 5.83 (s, $\eta\text{-}C_5H_5$); $^{13}C$ n.m.r. ($CDCl_3$) $\delta$ 32.90 ($ZrCH_2CH_2$, $J_{C-H}$ 124 Hz), 44.66 ($ZrCH_2$, $J_{C-H}$ 119 Hz), 76.61 ($OCH_2$, $J_{C-H}$ 139 Hz), and 109.61 p.p.m. ($\eta\text{-}C_5H_5$, $J_{C-H}$ 168 Hz)]. The mass spectra of (**1a—c**) exhibit $2M^+$ peaks which support the proposed dimeric structures. The spectral data, however, could not be used to rule out the ten-membered metallacycle (**3**). This was precluded by the following experimental evidence. The $^1H$ n.m.r. spectrum of (**1a**) in the presence of 0.25 equiv. of anhydrous $BF_3$ in $CDCl_3$ contains resonance of three kinds of methylene protons at $\delta$ 1.28 (t, $J$ 6.2 Hz), 2.10 (m), and 3.74 (t, $J$ 5.5 Hz) and a singlet at $\delta$ 5.99 due to the 1 : 1 complex of the monomer of (**1a**) and $BF_3$, in addition to those of free (**1a**). This is consistent with the assigned dimeric structure (**1**).† The structure of (**1c**) was unequivocally established by a single crystal *X*-ray analysis.



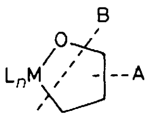
(**1**) a; $R^1=R^2=R^3=H$
b; $R^1=Me, R^2=R^3=H$
c; $R^1=R^2=H, R^3=Me$
d; $R^1=H, R^2=R^3=D$



(**2**) a; $n=1, R=H$
b; $n=1, R=Me$
c; $n=2, R=H$



(**3**)



(**4**)

*Crystal data:* $C_{28}H_{36}O_2Zr_2$, $M = 558.98$, monoclinic, space group $P2_1/n$, $a = 17.090(4)$, $b = 8.345(3)$, $c = 8.841(3)$ Å, $\beta = 102.90(2)°$, $U = 1228.9(6)$ Å$^3$, $Z = 2$, $D_c = 1.51$ g cm$^{-3}$. Data were collected ($2\theta_{max} = 60°$) on a Rigaku AFC-5 four circle diffractometer using Mo-$K_\alpha$ radiation (graphite monochromator) and a $\theta$–$2\theta$ scan technique. 2030 Independent reflections with $|F| > 3\sigma(F)$ were used in the refinement and an absorption correction (with $\mu = 8.56$ cm$^{-1}$) was applied. The structure was solved by heavy-atom methods and refined by block-diagonal least-squares. The atoms were refined anisotropically except for the hydrogen atoms, which were refined isotropically. The current $R$ value is 0.039 ($R_w$ 0.044).‡

The complex (**1c**) has a dimeric structure as in Figure 1. The two halves of the dimer are related by a crystallographic

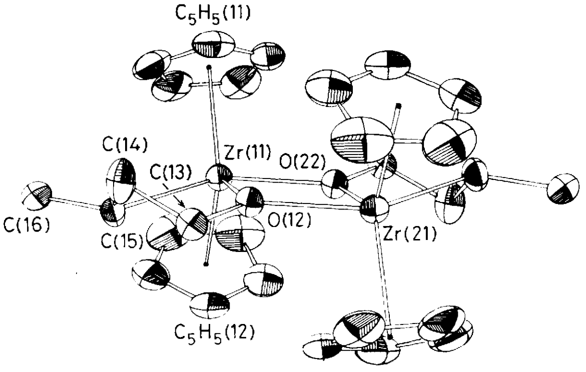


**Figure 1.** A perspective view of one of the independent dimeric molecules of (**1c**). The hydrogen atoms are omitted for simplicity. The carbon atoms C(13)–C(16) have an occupancy probability of 0.5 owing to positional disorder. Some important bond lengths and angles: Zr(11)–O(12) 2.190(3), Zr(11)–O(22) 2.234(7), O(12)–C(13) 1.427(10), C(13)–C(14) 1.506(16), C(14)–C(15) 1.503(17), C(15)–C(16) 1.559(17), Zr(11)–C(15) 2.382(11), Zr(11)–$C_5H_5(11)$ (centroid) 2.265, Zr(11)–$C_5H_5(12)$ (centroid) 2.274 Å; O(12)–Zr(11)–C(15) 72.2(4), O(12)–Zr(11)–O(22) 64.5(4), $C_5H_5(11)$ (centroid)–Zr(11)–$C_5H_5(12)$ (centroid) 125.8°.

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† Complexation of one of the two oxygen atoms of (**3**) with $BF_3$ will give rise to six magnetically inequivalent methylenes, and hence we would expect to observe n.m.r. absorptions of these methylene protons and those of the free complex (**3**).

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

inversion centre. Each zirconium atom has a five co-ordinated bent metallocene structure.

Thermal decompositions of (**1a**—**c**) at 240—250 °C *in vacuo* have been carried out. The complex (**1a**) afforded methane (2%), ethylene (19%), and propene (79%) in addition to cyclopentadiene.§ The yield of cyclopentadiene varied depending on the reaction conditions. The decomposition of (**1b**) gave methane (7%), propene (89%), 2-methylpropene (4%), and cyclopentadiene, while (**1c**) produced methane (7%), propene (21%), butane (2%), but-1-ene (50%), (*E*)-but-2-ene (5%), (*Z*)-but-2-ene (5%), and buta-1,3-diene (9%) accompanied by cyclopentadiene. The thermal decomposition of 2-[di(cyclopentadienyl)zircona]-1-oxa[3,3-$^2H_2$]-cyclopentane (**1d**) followed by careful analyses of the products by $^1H$ (400 MHz), $^2H$ (61 MHz), and $^{13}C$ (100 MHz) n.m.r. indicated the formation of methane (11%), [$^2H_2$]-ethylene (30%), [1,1-$^2H_2$]propene (23%), and [3,3-$^2H_2$]-propene (35%). The deuterium content of the methane was not determined. The i.r. spectrum of the decomposition residue exhibited an intense broad absorption between 720—780 cm$^{-1}$ assigned to $\nu_{Zr-O-Zr}$ and the corresponding $^1H$ n.m.r. spectrum showed a singlet at $\delta$ 6.34 which indicate that an oxygen-bridged oligomer of $(\eta\text{-}C_5H_5)_2Zr{=}O$ had been formed.[5] The above experimental results suggest that the thermal ring fission of (**1**) occurs mainly in two modes, A and B [see (**4**)]. Mode A involves a $\beta$-carbon–carbon bond fission which corresponds formally to the retro-olefin insertion from (**1**) to give the complex $(\eta\text{-}C_5H_5)_2Zr(\text{olefin})(\eta^2\text{-}O{=}CH_2)$. The reverse reactions in which olefins add to the complexes $(\eta\text{-}C_5H_5)_2M(\eta^2\text{-}O{=}CRR')$ (M = Ti or Zr) to give five-membered oxametallacycles are well established.[1c,2] The $(\eta^2\text{-}O{=}CH_2)$zirconocene complex possibly formed by mode A fission may suffer further thermal decomposition under the reaction conditions as has been reported for the cyclotrimer of $(\eta^2\text{-}O{=}CH_2)$zirconocene.[2c] The formation of a three-carbon unit from (**1a**) and four-carbon units from (**1b**) and (**1c**) (mode B reaction) can reasonably be accounted for by sequential reactions which involve an initial intramolecular retro-hydrozirconation followed by cleavage of the allylic C–O bond forming a $(\eta\text{-}C_5H_5)_2Zr(O)(H)(CH_2CHCH_2)$ type complex and a final reductive elimination of the hydrocarbons.¶**

The characteristic behaviour of 1-oxa-2-zirconacyclopentanes can be attributed to the marked oxaphilic nature of the group 4 transition metals.

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§ Yields of the volatile products except those of cyclopentadiene are given in mole%. Good mass balances were obtained for (**1a**—**d**).

¶ If a 1,3-diradical species was intermediate, cyclopropane derivatives and internal alkenes would be the major products (ref. 6).

** It has been suggested that 1-alkenes are predominantly formed from (1,2-dialkyl-substituted $\eta^3$-allyl)hydridotantalum complexes *via* $\eta^1$-allyl complexes (ref. 7).