

Intramolecular Interactions in Bis(pentamethylcyclopentadienyl) Complexes: X-Ray Structures of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{OH})(\text{Cl})$ and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{OH})_2$

Roberto Bortolin, Vikram Patel, Ian Munday, Nicholas J. Taylor, and Arthur J. Carty*

Guelph-Waterloo Centre for Graduate Work in Chemistry, Waterloo Campus, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

The structures of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{OH})(\text{Cl})$ (**1**) and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{OH})_2$ (**2**) have been determined by X-ray diffraction; location of all hydrogen atoms in (**1**) has established the presence of significant intramolecular non-bonding contacts and (**2**) is the first early transition metal dihydroxo complex to be structurally characterized.

Use of the $\eta^5\text{-C}_5\text{Me}_5$ ligand, a bulky group with strong donor characteristics, has led to the development of new chemistry not accessible *via* the corresponding cyclopentadienyl derivatives.¹ An interesting example is a comparison of the reactions of $(\eta^5\text{-C}_5\text{R}_5)_2\text{Zr}(\text{Me})_2$ and $(\eta^5\text{-C}_5\text{R}_5)_2\text{Zr}(\text{Me})(\text{Cl})$ with water which afford, for R=H the well known oxo-bridged dimers

$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{X})]_2\text{O}$ (X=Me, Cl)² and for R=Me, compounds which have recently been formulated by Bercaw and co-workers³ as $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{OH})(\text{Cl})$ (**1**) and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{OH})_2$ (**2**). The failure of (**1**) and (**2**) to dimerise with loss of H₂O might be attributed to steric factors. We had independently synthesised (**1**) and (**2**) as precursors of the

monomeric oxozirconium complex $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrO}$ and determined the structures of both compounds. The *X*-ray analysis of (1) is highly accurate and the location of all hydrogen atoms in the structure presented a rare opportunity to assess the extent of intramolecular interactions in a bent bis(pentamethylcyclopentadienyl) compound. Significant inter-ring and ring-anion interactions are present in (2) and (1) which are detailed herein. Although a few monomeric organometallic hydroxo compounds have been previously described⁴ and hydroxo species are important intermediates in a number of catalytic⁵ and biological processes,⁶ few have been structurally authenticated⁷ and the *X*-ray analysis of (2) is the first for a monomeric dihydroxo transition metal organometallic complex.

$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{OH})(\text{Cl})$ (1) and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{OH})_2$ (2) were synthesised in 85 and 90% yield *via* treatment of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{Bu}^n)(\text{Cl})$ and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{Me})_2$ with one and two equivalents of H_2O in hexane. The mass spectrum of (2) is interesting, showing a parent ion at *m/z* 394 (⁹⁰Zr) and an intense ion at *m/z* 376 corresponding to the oxozirconium cation $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr=O}]^+$. Confirmation of the identity of (1) and (2) as discrete, monomeric hydroxo compounds was provided by single crystal *X*-ray diffraction studies.† ORTEP plots of the structures are shown in Figures 1 and 2. In both molecules the zirconium atom is co-ordinated to two $\eta^5\text{-C}_5\text{Me}_5$ groups and two ancillary ligands, one chloro and one hydroxo group in (1) and two hydroxo ligands in (2) with the centroids of the two C_5Me_5 rings and the two OH (or OH and Cl) ligands defining a severely distorted tetrahedral stereochemistry at the metal. There are significant structural differences between (1) and (2) and other bent pentamethylzirconocene derivatives. Thus the O–Zr–Cl [98.8(1)°] and O(1)–Zr–O(2) [99.7(3)°] angles in (1) and (2) are much larger than the corresponding L–Zr–L angles in $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrL}_2]\text{N}_2$ (L = N_2 ,⁸ av. 87.1°) and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrL}_2$ (L = CO,⁹ 86.3°) while the angles involving the centroids of the C_5Me_5 rings [137.9° in (1) and 137.6° in (2)] are much smaller {*cf.* 141.3° in $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrN}_2]_2\text{N}_2$;⁸ 147.4° in $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CO})_2$ }⁹ resulting in closer methyl–methyl contacts (Figure 1) in the hydroxo complexes. Indeed in (1) the H(15b)–H(20b) distance of 2.08 Å is well inside twice the van der Waals radius of hydrogen (1.20 Å). There are also relatively short contacts

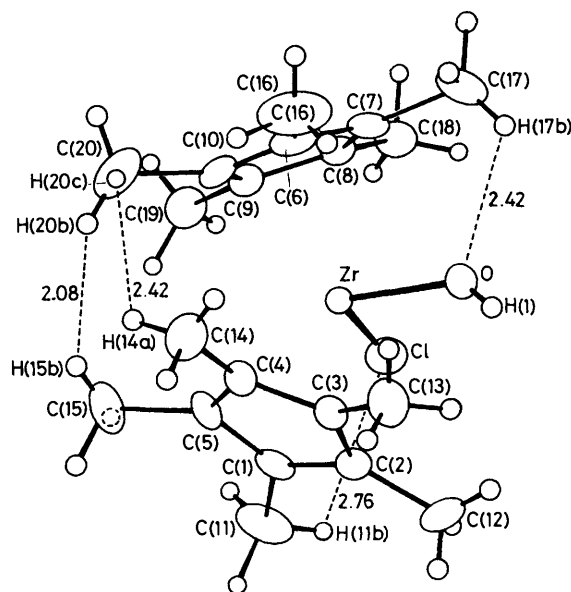


Figure 1. The molecular structure of (1), $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{OH})(\text{Cl})$, showing all the hydrogen atoms. Short intramolecular contacts are shown. Other important parameters: Zr–Cl 2.4776(8), Zr–O 1.950(2), Zr–C [C(1)–C(5)] av. 2.556, Zr–C [C(6)–C(10)] av. 2.565 Å; Cl–Zr–O 98.8(1)°.

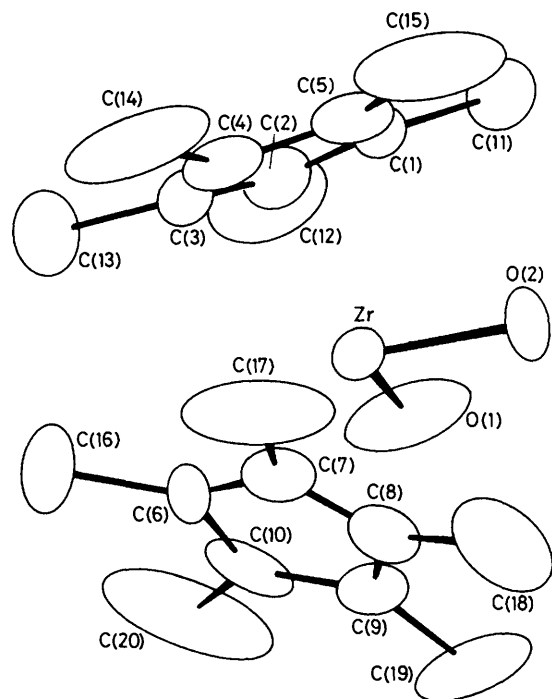


Figure 2. The structure of (2), $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{OH})_2$ showing the atomic numbering. Important parameters are: Zr–O(1) 1.975(8), Zr–O(2) 1.982(7), Zr–C [C(1)–C(5)] av. 2.549, Zr–C [C(6)–C(10)] av. 2.550 Å; O(1)–Zr–O(2) 99.7(3)°; O(1)···O(1') 3.117(13), O(2)···O(2') 3.246(10) Å.

† *Crystal data:* Compound (1) $\text{C}_{20}\text{H}_{31}\text{ClOZr}$, $M = 414.14$, monoclinic, space group $P2_1/c$, $a = 13.826(1)$, $b = 8.511(1)$, $c = 17.988(2)$ Å, $\beta = 109.54(1)^\circ$, $U = 1994.8(4)$ Å³; $Z = 4$, $D_c = 1.379$ g cm⁻³; $F(000) = 864$; $\lambda = 0.71069$ Å; $\mu(\text{Mo-K}\alpha) = 6.79$ cm⁻¹. The intensities of 3546 independent reflections measured on a crystal of dimensions $0.28 \times 0.33 \times 0.34$ mm using θ – 2θ scans on a Syntex P₂₁ diffractometer with Mo- $K\alpha$ radiation ($\lambda = 0.71069$ Å) afforded 2951 unique observed data [$I \geq 3\sigma(I)$] which were used to solve and refine the structure by Patterson, Fourier, and full-matrix least-squares methods. With anisotropic coefficients for all non-hydrogen atoms and isotropic parameters for all hydrogen atoms refinement converged at $R = 0.025$, $R_w = 0.030$. All hydrogen atoms were located in this precise structure.

Compound (2) $\text{C}_{20}\text{H}_{32}\text{O}_2\text{Zr}$, $M = 395.70$, monoclinic, space group $P2_1/n$, $a = 8.590(1)$, $b = 21.563(3)$, $c = 10.960(2)$ Å, $\beta = 102.88(1)^\circ$, $U = 1979.0(4)$ Å³; $\mu(\text{Mo-K}\alpha) = 5.56$ cm⁻¹. Intensity data were collected on a crystal of dimensions ~ 0.3 mm³ encased in epoxy resin using θ – 2θ scans ($3.2 < 2\theta \leq 50^\circ$). The structure solution and refinement were based on 2340 unique observed [$I \geq 3\sigma(I)$] reflections. Full-matrix least-squares refinement (anisotropic thermal parameters) for all non-hydrogen atoms converged at $R = 0.057$, $R_w = 0.068$. 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.

between methyl hydrogen atoms H(17b) and O (2.42 Å) and H(11b) and Cl (2.76 Å). An analysis of intra- and intermolecular contacts in (1) did not reveal significant O–H···Cl or O–H···O hydrogen bonding; for (2), the intermolecular distances O(1)···O(1') [3.117(13) Å] and O(2)···O(2') [3.246(10) Å] lie outside the limit of ~ 2.80 Å for O–H···O bonding and the intramolecular O(1)···O(2) distance

[3.025(12) Å] is imposed by the short Zr–O bond lengths [1.950(2) Å in (1); av. 1.978 in (2)] and O–Zr–O angle [99.7(3)°]. When compared to the Zr–Cl distance of 2.4776(8) Å in (1) the Zr–O bond lengths in (1) and (2) are notably foreshortened. This is a recurring feature of zirconium oxo-bridged dimers,¹⁰ trimers,^{11,12} and alkoxides¹³ and may be attributed to the remarkable oxophilicity of zirconium and $\pi(\text{O})-\text{d}\pi(\text{Zr})$ multiple bonding.

Figure 1 illustrates that the zirconium atom is well protected by the bulky C_5Me_5 ligands and this factor may account for the monomeric nature of these unusual hydroxo species, the lack of strong intermolecular hydrogen bonding, and their failure to dimerise with loss of water. These results suggest the possibility of stabilising other 'reactive' anionic ligands *via* co-ordination within the $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}$ cavity, a strategy which we are currently exploring.

We are grateful to the Natural Sciences and Engineering Research Council for support of this work *via* a Strategic Grant.

Received, 16th November 1984; Com. 1617

References

- 1 For a review see: P. M. Maitlis, *Coord. Chem. Rev.*, 1982, **43**, 377.
- 2 P. C. Wailes, R. S. P. Coutts, and H. Weigold, 'Organometallic Chemistry of Titanium, Zirconium and Hafnium,' Academic Press, New York, 1974, p. 132.
- 3 G. L. Hillhouse and J. E. Bercaw, *J. Am. Chem. Soc.*, 1984, **106**, 5472.
- 4 See for example: T. G. Appleton and M. A. Bennett, *J. Organomet. Chem.*, 1973, **55**, C88; J. Peone, Jr. and L. Vaska, *Chem. Commun.*, 1971, 418. Hydroxo bridged compounds are known: see for example A. Nutton, P. M. Bailey, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1981, 1997.
- 5 C. K. Rofer De Poorter, *Chem. Rev.*, 1981, **81**, 447; A. Brenner and D. A. Hucul, *J. Am. Chem. Soc.*, 1980, **102**, 2484; H. Mimoun, M. M. P. Machirant, and I. Serec de Roch, *J. Am. Chem. Soc.*, 1978, **100**, 5437.
- 6 S. Lindskog in 'Advances in Inorganic Biochemistry,' eds. G. L. Eichhorn and L. G. Marzilli, Elsevier Biomedical, 1982, ch. 4.
- 7 K. Prout, T. S. Cameron, R. A. Forder, S. R. Critchley, B. Denton, and G. V. Rees, *Acta Crystallogr., Sect. B.*, 1974, **30**, 2290.
- 8 R. D. Sanner, J. M. Manriquez, R. E. Marsh, and J. E. Bercaw, *J. Am. Chem. Soc.*, 1976, **98**, 8351.
- 9 D. J. Sikora, M. D. Rausch, R. D. Rogers, and J. L. Atwood, *J. Am. Chem. Soc.*, 1981, **103**, 1265.
- 10 J. L. Petersen, *J. Organomet. Chem.*, 1979, **106**, 179.
- 11 P. T. Barger, B. D. Santasiero, J. Armantrout, and J. E. Bercaw, *J. Am. Chem. Soc.*, 1984, **106**, 5178.
- 12 G. Fachinetti, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Am. Chem. Soc.*, 1979, **101**, 1767.
- 13 T. V. Lubben, P. T. Wolczanski, and G. D. Van Duyne, *Organometallics*, 1984, **3**, 977.