

**Polynuclear Pentamethylcyclopentadienyl Chloro, Oxo, and Hydroxo Zirconium(IV) Complexes; X-Ray structure of  $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}\}_3(\mu\text{-Cl})_4(\mu_3\text{-O})]$  and  $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}_2(\text{H}_2\text{O})(\mu\text{-OH})\}_2]$**

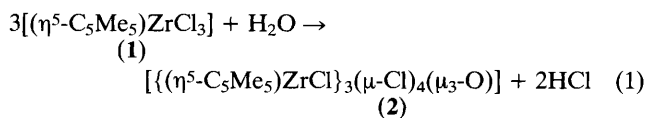
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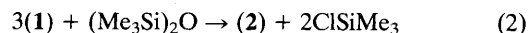
$[(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}_3]$  (**1**) Can be hydrolysed in toluene to give  $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}\}_3(\mu\text{-Cl})_4(\mu_3\text{-O})]$  (**2**) while the reaction of (**1**) with LiOH·H<sub>2</sub>O in tetrahydrofuran (thf) gives  $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}_2(\text{H}_2\text{O})(\mu\text{-OH})\}_2]$  (**4**); the structures of (**2**) and (**4**) have been determined by X-ray diffraction methods.

While the hydrolysis of different organotitanium compounds, leading to a variety of polynuclear  $\mu$ -oxo organoderivatives, has been studied in recent years,<sup>1</sup> very few reports about their heavier zirconium analogues have appeared.<sup>2</sup> We have recently studied the hydrolysis of pentamethylcyclopentadienyl titanium tri-alkyls and -halides, leading to several di-, tri- and tetra-nuclear species,<sup>1b,3</sup> and we disclose in this communication the initial steps of the hydrolysis of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}_3]$  (**1**). Controlled hydrolysis of (**1**) with a stoichiometric amount of water in toluene for 12 h at 80 °C gives the yellow trinuclear complex (**2**)<sup>†</sup> in ca. 70% yield according to equation 1



Compound (**2**) can also be obtained from the reaction between (**1**) and hexamethyldisiloxane under the same conditions as above, chlorotrimethylsilane being liberated on this occasion [equation (2)] and also, rather unexpectedly, in the reaction between  $[(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}_3(\text{H}_2\text{O})_2]$  and two equivalents of trimethylaluminium in toluene.

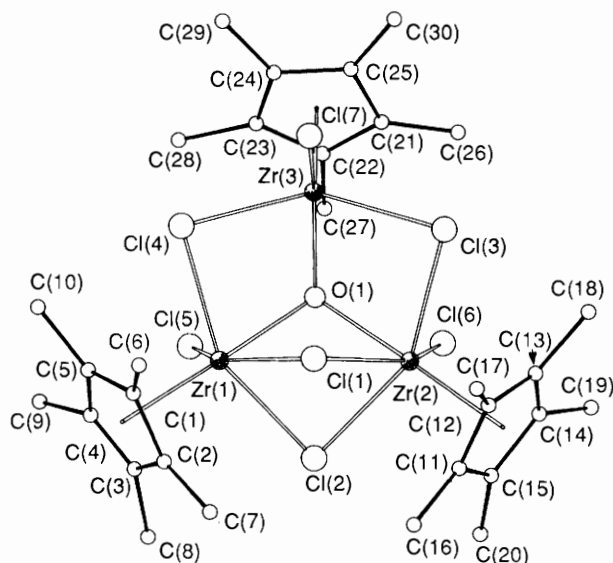
<sup>†</sup> Satisfactory analytical data for the new complexes were obtained. (**2**): <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  2.09; <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  125.6 and 13.0; IR (Nujol mull)  $\nu(\text{Zr-O})$  589vs cm<sup>-1</sup>. (**4**): IR (Nujol mull)  $\nu(\text{OH})$  3533m,  $\nu(\text{OH}_2)$  3354m,br,  $\delta(\text{ZrOH})$  1609w,  $\nu(\text{ZrOZr})$  728m, 719s cm<sup>-1</sup>.



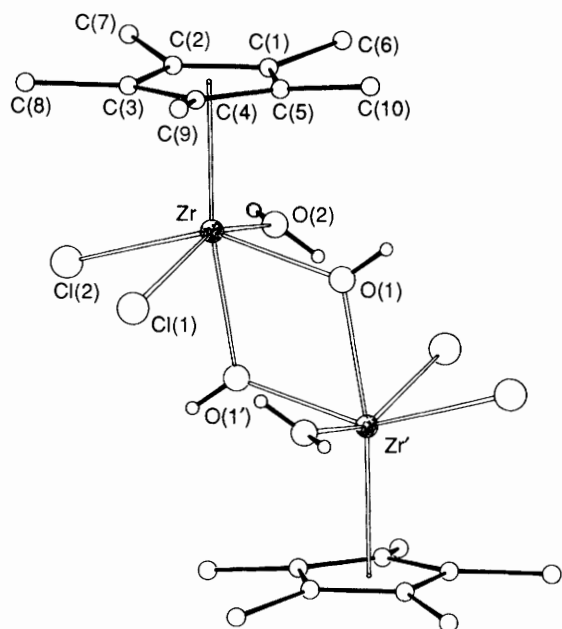
The structure of (**2**), represented in Figure 1, has been determined by X-ray diffraction methods.<sup>‡</sup> The complex, having an approximately C<sub>s</sub> symmetry, consists of three  $(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}$  fragments with three Zr atoms at the vertices

<sup>‡</sup> Crystal data for  $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}\}_3(\mu\text{-Cl})_4(\mu_3\text{-O})]$  (**2**): C<sub>30</sub>H<sub>45</sub>Cl<sub>7</sub>OZr<sub>3</sub>, *M* = 943.52, monoclinic, space group Cc, *a* = 11.906(3), *b* = 20.789(5), *c* = 16.267(8) Å,  $\beta$  = 108.78(2)°, *U* = 3812(2) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.644 g cm<sup>-3</sup>, *F*(000) = 1888, graphite-monochromated Mo-K $\alpha$  radiation,  $\lambda$  = 0.71073 Å,  $\mu$  = 13.11 cm<sup>-1</sup>.

For  $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}_2(\text{H}_2\text{O})(\mu\text{-OH})\}_2]$  (**4**): C<sub>20</sub>H<sub>36</sub>Cl<sub>4</sub>O<sub>4</sub>Zr<sub>2</sub>, *M* = 664.75, monoclinic, space group P2<sub>1</sub>/*n*, *a* = 8.343(1), *b* = 8.816(2), *c* = 18.254(3) Å,  $\beta$  = 96.07(1)°, *U* = 1335.1(4) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.654 g cm<sup>-3</sup>, *F*(000) = 672, graphite-monochromated Mo-K $\alpha$  radiation,  $\lambda$  = 0.71073 Å,  $\mu$  = 11.95 cm<sup>-1</sup>. The intensity data for both compounds were collected on a CAD4 Enraf-Nonius diffractometer, using the  $\omega$ -2 $\theta$  scan technique at room temperature; 3341 (**2**) and 2900 (**4**) unique reflections were measured (with  $\theta$  in the range 3–25° (**2**) and 3–27° (**4**)); 2935 (**2**) and 1642 (**4**), having *I* > 2 $\sigma$ (*I*), were used in the refinement. The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures, with anisotropic thermal parameters in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms were introduced in calculated positions [excepting those at O(1) and O(2) of (**4**), which were clearly localized and refined] and refined 'riding' on the carbon atoms. The *R* and *R*<sub>w</sub> values were 0.0487 and 0.0661 for (**2**), 0.0257 and 0.0334 for (**4**). Atomic co-ordinates, thermal parameters, and a complete list of bond distances and angles have been deposited at Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**Figure 1.** View of the molecular structure of (2). Selected bond distances (Å) and angles (°): Zr(1)–O(1) 2.165(8), Zr(2)–O(1) 2.163(9), Zr(3)–O(1) 2.003(9), Zr(1)–Cl(1) 2.668(3), Zr(1)–Cl(2) 2.581(4), Zr(1)–Cl(4) 2.607(5), Zr(1)–Cl(5) 2.426(4), Zr(2)–Cl(1) 2.689(4), Zr(2)–Cl(2) 2.585(3), Zr(2)–Cl(3) 2.585(4), Zr(2)–Cl(6) 2.410(5), Zr(3)–Cl(3) 2.563(4), Zr(3)–Cl(4) 2.546(4), Zr(3)–Cl(7) 2.436(5), Zr(1)–Cp(1) 2.26(2), Zr(2)–Cp(2) 2.24(2), Zr(3)–Cp(3) 2.20(1), Zr(1)–O(1)–Zr(2) 107.0(4), Zr(1)–O(1)–Zr(3) 116.5(4), Zr(2)–O(1)–Zr(3) 117.5(4) [Cp(*n*) = centroid of C<sub>5</sub>Me<sub>5</sub> ring attached to Zr(*n*)].

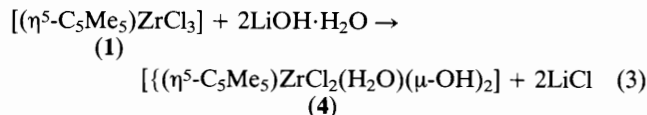


**Figure 2.** View of the molecular structure of (4). Selected bond distances (Å) and angles (°): Zr–O(1) 2.081(3), Zr–O(2) 2.246(3), Zr–O(1') 2.232(3), Zr–Cl(1) 2.514(1), Zr–Cl(2) 2.533(1), Zr–Cp(1) 2.238(5), Zr–O(1)–Zr' 114.0(1).

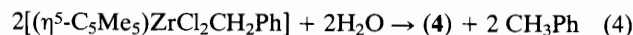
of an isosceles triangle [Zr(1) ··· Zr(2) ··· 3.478(2), Zr(1) ··· Zr(3) 3.545(2), and Zr(2) ··· Zr(3) 3.562(3) Å]. The two longest edges are bridged by a chlorine atom, a double chlorine bridge is disposed on the shortest edge, and an

oxygen atom caps the Zr triangle. The O(1), Cl(2), Cl(5), Cl(6) atoms, and the (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(3) ring are situated on the same side with respect to the Zr triangle, while the Cl(1), Cl(3), Cl(4), Cl(7) atoms, and the (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(1) and (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(2) rings are on the opposite side. This arrangement is similar to that found in [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)MCl]<sub>3</sub>(μ-Cl)(μ-O)<sub>3</sub>(μ<sub>3</sub>-O)] (M = Nb, Ta).<sup>4</sup> Taking the centroid of the C<sub>5</sub>Me<sub>5</sub> rings as occupying one co-ordination site, Zr(1) and Zr(2) are in a distorted octahedral environment while Zr(3) is in a distorted bipyramidal trigonal one. The electronic unsaturation and less crowded environment of Zr(3) relative to Zr(1) and Zr(2) may be related to the facts that: (i) O(1) is 0.16 Å closer to Zr(3) than to the other metal atoms, and (ii) the bridging Cl–Zr(3) distances are the shortest among all the (μ-Cl)–Zr bonds. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of (2) at room temperature indicate that a dynamic process, which is being further studied, might take place in solution that interchanges the terminal and bridging chlorine atoms.

Complex (2) can be viewed as an adduct of [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)ZrCl<sub>3</sub>] (1) and the hypothetical [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)ZrCl(μ-Cl)]<sub>2</sub>(μ-O) (3), which in turn would be the product of the hydrolysis of the first Zr–Cl bond of (1). In fact, the electron impact mass spectrum of (2) does not show its molecular ion but instead shows those of (1) and (3) along with the species derived from their fragmentation. It is well known that many μ-oxo metallo compounds are formed by the condensation of hydroxo derivatives with water elimination, and what could be viewed as the hydroxide precursor of (3), in the form of its dimerized water adduct, can be obtained in 45–50% yield from the reaction of (1) and wet lithium hydroxide in thf according to equation (3):



Complex (4)<sup>†</sup> is also the hydrolysis product of dihalopentamethylcyclopentadienyl zirconium alkyls (alkyl = benzyl, trimethylsilylmethyl), e.g. equation (4).



The expected IR and NMR behaviour was observed for (4). Its X-ray<sup>‡</sup> determination (Figure 2) shows it to be the dimer of [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)ZrCl<sub>2</sub>(OH)(H<sub>2</sub>O)], which should be formally the water adduct of the first product arising in the hydrolytic sequence of (1). The dimer is centrosymmetric and exhibits the trapezoidal Zr<sub>2</sub>(μ-OH)<sub>2</sub> system found in several zirconium inorganic basic salts<sup>5</sup> and monocyclopentadienyl hydroxo complexes.<sup>2a,b</sup> The metal atom can be considered as having a distorted octahedral environment and the Zr–OH distance to the hydroxide group *trans* to the C<sub>5</sub>Me<sub>5</sub> ring is 0.15 Å longer than the *cis*; it is close to the Zr–OH<sub>2</sub> distance [Zr–O(1) 2.081(3), Zr–O(1') 2.232(3), and Zr–O(2) 2.246(3) Å]. The 0.15 Å difference in distance between Zr and the bridging oxygens of the hydroxide groups is notably higher than in the reported Zr<sub>2</sub>(μ-OH)<sub>2</sub> systems, in which it ranges from 0.06 to 0.08 Å.<sup>2a,2b,5</sup> An intramolecular hydrogen bond involves the oxygen atom O(2) of the water molecule and the chlorine atom Cl(1) [O(2)–H ··· Cl(1) = 3.060(3) Å; O(2)–H–Cl(1) 161(6)°].

Complexes (2) and (4) can be considered the earliest products arising in the hydrolytic sequence of (1), that subsequently leads to [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)ZrCl]<sub>3</sub>(μ-OH)<sub>3</sub>(μ<sub>3</sub>-OH)(μ<sub>3</sub>-O)], which can be obtained in thf with two equivalents of water and triethylamine and whose structure has been recently reported.<sup>2c</sup>

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### References

- 1 (a) For a review see, L. Sutin and F. Bottomley, *Adv. Organomet. Chem.*, 1988, **28**, 339; (b) F. Palacios, P. Royo, R. Serrano, J. L. Balcázar, I. Fonseca, and F. Florencio, *J. Organomet. Chem.*, 1989, **375**, 51 and references therein.
  - 2 (a) W. Lasser and U. Thewalt, *J. Organomet. Chem.*, 1984, **275**, 63; (b) W. Lasser and U. Thewalt, *ibid.*, 1986, **311**, 69; (c) L. M. Babcock, V. W. Day, and W. G. Klemperer; *Inorg. Chem.*, 1989, **28**, 806.
  - 3 S. García-Blanco, M. P. Gómez-Sal, S. Martínez-Carreras, M. Mena, P. Royo, and R. Serrano, *J. Chem. Soc., Chem. Commun.*, 1986, 1572.
  - 4 (a) P. Jernakoff, C. M. de Bellefon, G. L. Geoffroy, A. L. Rheingold, and S. J. Geib, *New J. Chem.*, 1988, **12**, 329; (b) J. de la Mata, R. Fandos, M. Gómez, P. Gómez, S. Martínez, and P. Royo, *Organometallics*, accepted for publication.
  - 5 (a) P. B. Wawhan and G. Lundgreen, *Inorg. Chem.*, 1966, **5**, 284; (b) T. C. W. Mak, *Can. J. Chem.*, 1968, **46**, 349; (c) Y. E. Grobunova, V. G. Kuznetsor, and E. S. Kosaleva, *Russ. J. Struct. Chem.*, 1968, **9**, 815.
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