

## Polynuclear Organometal Oxides: Synthesis and Structure of $[(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}]_3(\mu_3\text{-O})(\mu_3\text{-OH})(\mu\text{-OH})_3\cdot 2\text{THF}$ (THF = Tetrahydrofuran)

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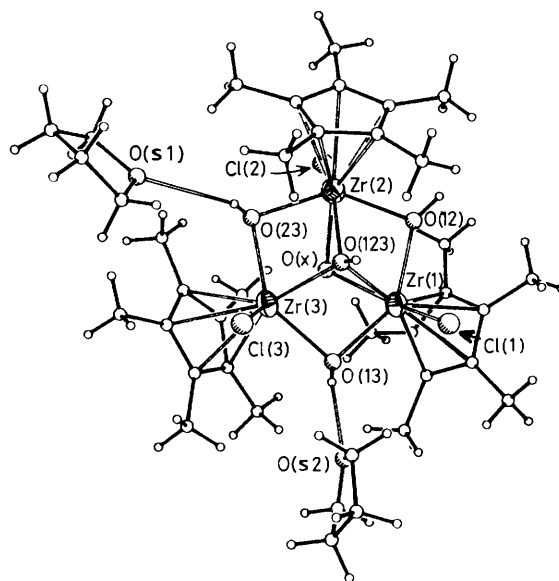
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Base hydrolysis of  $(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}_3$  in tetrahydrofuran (THF) yields  $[(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}]_3(\text{O})(\text{OH})_4\cdot 2\text{THF}$  which, according to X-ray structural analysis, contains a triangular  $\text{Zr}_3$  core capped above and below by  $\mu_3\text{-O}$  and  $\mu_3\text{-OH}$  groups and edge-bridged by three  $\mu_2\text{-OH}$  groups.

Early transition metal polyoxoanions have been shown to have an extensive organic and organometallic reaction chemistry.<sup>1</sup> The systems investigated thus far, however, lack two important features known to influence solid oxide surface reactivity, namely, accessible Lewis acidic metal centres and basic hydroxy groups.<sup>2</sup> In order to prepare soluble metal oxides having these features, we have initiated an investigation of polynuclear, group IV organometal oxides.<sup>3</sup> We report here the synthesis and structure of a highly reactive, hydrocarbon-soluble species,  $[(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}]_3(\text{O})(\text{OH})_4\cdot 2\text{THF}$  (THF = tetrahydrofuran).

Reaction of  $(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}_3$  with water (2 equiv.) and triethylamine (2 equiv.) in THF solution followed by filtration, removal of solvent, crystallization from THF, and drying *in vacuo*, gave  $[(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}]_3(\text{O})(\text{OH})_4\cdot 2(\text{OC}_4\text{H}_8)$  in 61% yield.<sup>†</sup> X-Ray structural analysis of this THF solvate revealed the presence of a cluster containing a nearly equilateral triangular core of three Zr atoms capped above and below by  $\mu_3\text{-O}$  and  $\mu_3\text{-OH}$  groups and symmetrically edge bridged by three  $\mu_2\text{-OH}$  groups whose oxygen atoms are coplanar to within 0.07 Å with the three Zr atoms (see Figure 1).<sup>‡</sup> The pseudo-octahedral co-ordination sphere at each Zr atom is completed by a terminally bonded chloride and a  $\pi$ -bonded  $(\eta^5\text{-C}_5\text{Me}_5)$  ligand, yielding a cluster geometry remarkably similar to that of  $\text{Mo}_3(\mu_3\text{-O})(\mu_3\text{-OR})(\mu\text{-OR})_3(\text{OR})_6$ , R = isopropyl and neopentyl,<sup>4</sup> and  $\{[(\eta^5\text{-C}_5\text{Me}_5)\text{Ta}]_3(\mu_3\text{-O})_2(\mu\text{-O})_3\text{Cl}(\text{H}_2\text{O})_2\}\text{Cl}$ .<sup>5</sup> Two of the terminal chloride ligands and one of the  $(\eta^5\text{-C}_5\text{Me}_5)$  ligands lie on one side of the  $(\text{-Zr-OH-})_3$  ring while the remaining chloride and  $(\eta^5\text{-C}_5\text{Me}_5)$  ligands lie on the opposite side to give a molecule which approximates  $C_s$ -*m* symmetry. The Zr-Cl, Zr-C, ring

C-C, ring C-Me, and Zr-( $\mu_2\text{-OH}$ ) bond lengths average § 2.477 (2, 8, 11, 3), 2.545 (7, 16, 45, 15), 1.404 (11, 8, 20, 15), 1.508 (11, 11, 26, 15), and 2.147 (4, 9, 13, 6) Å, respectively, and are similar to those previously observed in  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrCl}(\text{OH})$ ,<sup>6</sup>  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrN}_2]_2\text{N}_2$ ,<sup>7</sup> and  $\text{Zr}_2(\text{OH})_2(\text{SO}_4)_3(\text{H}_2\text{O})_4$ .<sup>8</sup> The Zr-O bonds to the  $\mu_3\text{-O}$  and  $\mu_3\text{-OH}$  oxygens *trans* to the  $(\eta^5\text{-C}_5\text{Me}_5)$  ligands are at least 0.08 Å longer than the corresponding bonds *trans* to the chloride ligands (see Figure 1 caption). A similar lengthening of Zr-( $\mu\text{-OH}$ ) bonds *trans* to a  $(\eta^5\text{-C}_5\text{H}_5)$  ligand is observed in  $[(\eta^5\text{-C}_5\text{H}_5)\text{Zr}(\kappa^2\text{-O-NO}_3)_2(\mu\text{-OH})]_2$ .<sup>9</sup> The *trans*-( $\eta^5\text{-C}_5\text{Me}_5$ )-Zr-O bond angles average 173.5 (—, 6, 8, 3)°.



**Figure 1.** Perspective ORTEP plot of the solid-state structure for the  $[(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}]_3(\mu_3\text{-O})(\mu_3\text{-OH})(\mu\text{-OH})_3$  molecule as the THF solvate. The Zr atoms are labelled 1–3 and are represented by 50% thermal vibration ellipsoids. Chlorine and oxygen atoms are represented by large and medium-sized shaded spheres while carbon and hydrogen atoms are represented by medium-sized and small open spheres, respectively. The  $\mu_3\text{-O}$  and  $\mu_3\text{-OH}$  ligands are labelled O(x) and O(123), respectively. The Zr( $\mu_3\text{-O}$ ) bond distances are as follows: Zr(1)-O(123), 2.296(4), Zr(2)-O(123), 2.198(4), Zr(3)-O(123), 2.336(4), Zr(1)-O(x), 2.113(4), Zr(2)-O(x), 2.196(4), Zr(3)-O(x), 2.092(4) Å. The  $\mu_2\text{-OH}$  ligands are labelled O(12), O(13), and O(23); the hydrogen atoms on O(13) and O(23) are hydrogen bonded in the lattice to THF oxygen atoms.

<sup>†</sup>  $[(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}]_3(\mu_3\text{-O})(\mu_3\text{-OH})(\mu\text{-OH})_3\cdot 2(\text{OC}_4\text{H}_8)$ : satisfactory elemental analysis (C, H, Zr, Cl); i.r. (mineral oil)  $\nu(\text{Zr-OH})$  3655m, 3618m, 3520m, 3425m  $\text{cm}^{-1}$ ,  $\nu(\text{Zr-O-Zr})$  730s  $\text{cm}^{-1}$ .

<sup>‡</sup> *Crystal data:*  $\text{C}_{38}\text{H}_{65}\text{Cl}_3\text{O}_7\text{Zr}_3$ ,  $M_r = 1013.95$ , orthorhombic, space group  $Pbca$  ( $D_{2h}^{15}$ , no. 61),  $a = 11.320(3)$ ,  $b = 17.212(3)$ ,  $c = 46.253(8)$  Å;  $U = 9012(3)$  Å<sup>3</sup>;  $Z = 8$ ;  $D_c = 1.495$  g/cm<sup>3</sup>;  $\mu(\text{Mo-K}\alpha) = 0.89$  mm<sup>-1</sup>; 8246 unique data having  $2\theta < 50.7^\circ$  were collected on a Nicolet PI autodiffractometer using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and full (0.9°-wide)  $\omega$  scans. The structure was solved using the 'heavy atom' technique and the resulting structural parameters have been refined using counter-weighted cascade block-diagonal least-squares techniques to  $R = 0.046$  and  $R_w = 0.052$  for 5036 independent reflections having  $I > 3\sigma(I)$ . These refinement cycles employed anisotropic thermal parameters for all nonhydrogen atoms and fixed isotropic thermal parameters for the hydrogen atoms of the methyl groups which were refined as rigid rotors with idealized sp<sup>3</sup> hybridization and a C-H bond length of 0.96 Å. The four hydroxy hydrogen atoms were located by a difference Fourier synthesis and refined as independent isotropic atoms. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers are the averaged and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements which are included in the averaged value.

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