

The $Zr_6Cl_{12}(PMe_2Ph)_6$ molecule revisited: a directed synthesis

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Abstract

A new method for preparing the compound formally assigned the composition $Zr_6Cl_{12}(PMe_2Ph)_6$ is described. The compound can now be obtained reproducibly in about 16% yield. A new crystalline form was obtained and fully characterized by X-ray crystallography, giving molecular dimensions in essential agreement with those previously reported. Crystal data: space group, $P\bar{1}$ with $a = 19.032(4)$, $b = 13.328(2)$, $c = 14.401(2)$ Å, $\alpha = 92.69(1)$, $\beta = 92.18(2)$, $\gamma = 108.01(3)^\circ$, $V = 3464(2)$ Å³, $Z = 2$. The possibility that hydrogen atoms may be attached to each of two faces of the Zr_6 octahedron is suggested and discussed.

Keywords: Crystal structures; Zirconium complexes

1. Introduction

Several years ago [1] workers in this laboratory obtained very minute quantities of $Zr_6Cl_{12}(PMe_2Ph)_6$, and showed by X-ray crystallography that it contained a Zr_6Cl_{12} core (a Zr_6 octahedron with a μ -Cl on each edge) to which one PMe_2Ph ligand was attached along each exterior extension of the four-fold symmetry axes. It was shown that, unlike the many Zr_6X_{12} containing compounds previously studied by Ziebarth and Corbett [2], the Zr_6 octahedron contained no central atom or atoms, with the possible exception of hydrogen. In order to address the many questions raised by this discovery, larger quantities of the compound were required, but unfortunately, it proved impossible to obtain more than occasional, minute yields by the original method.

We now wish to report that we have found a preparative method that reproducibly affords yields of about 16% based on $ZrCl_4$ as starting material. New physical data are also reported.

2. Experimental

2.1. Preparation of $Zr_6Cl_{12}(PMe_2Ph)_6$

In a 50 ml flask, $ZrCl_4$ (0.466 g, 2.0 mmol) was stirred in 20 ml of toluene while $(n-C_4H_9)_3SnH$ (1.10 ml, 4.2

mmol) was added dropwise. The reduction of $ZrCl_4$ was evidenced by the formation of a dark red–brown precipitate on the bottom and walls of the reaction flask. The precipitate was washed with a copious amount of toluene to remove any residual $(n-C_4H_9)_3SnH$ and 1.3 equiv. of PMe_2Ph (0.371 ml, 2.60 mmol) in 20 ml of toluene were added by cannula. The precipitate was immediately solubilized forming a dark red solution. Na/Hg (0.33 ml, 2 M) amalgam was added dropwise. The solution gradually changed from red to orange over a 12 h period. When no further color change was evident, the solution was filtered through a fine frit into a 50 ml Schlenk tube and was layered with 30 ml of hexanes. After the diffusion of hexanes was complete, the Schlenk tube was placed in a freezer ($-20^\circ C$). Plate-shaped dark red crystals appeared within one week. The crystals were collected, dissolved in fresh toluene, and recrystallized by slow diffusion of hexanes at room temperature. Large irregular-shaped crystals formed after 3 days. They were suitable for single-crystal X-ray diffraction study. The isolated crystalline yield was 97 mg (16%).

2.2. X-ray crystallography

A large orange–red crystal was wedged into a Lindemann capillary tube. The capillary was filled with degassed and dried mineral oil and sealed at both ends

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with epoxy cement. The capillary was mounted on the goniometer head of a Syntex P3/F diffractometer and the crystal was optically centered. A rotation photograph was taken and the $(2x, 2y)$ coordinates of 15 reflections were entered. The reflections were centered and indexed, and a triclinic cell was obtained. The lattice dimensions were verified by axial photography. The data were collected by the ω - 2θ scan method in the range $4 < 2\theta < 46^\circ$. The structure was solved by direct methods in the centrosymmetric space group $P\bar{1}$ (No. 2). Two independent sets of six heavy atoms were found from the Fourier map that followed the structure solution, each set around an inversion center. Thus, there are two crystallographically independent, centrosymmetric hexazirconium molecules (a and b) in the unit cell. The phosphine carbon atoms were found from difference Fourier maps that followed the isotropic refinement of the heavy atoms. All non-hydrogen atoms were then refined anisotropically to convergence. The final data to parameter ratio was 9. Hydrogen atoms were not included in the model refined.

Crystal data and figures of merit are given in Table 1. Selected bond distances and angles are listed in Table 2. A drawing of one of the two molecules is shown in Fig. 1. See also Supplementary material.

Table 1
Crystal data for $Zr_6Cl_{12}(PMe_2Ph)_6$

Formula	$Zr_6Cl_{12}P_6C_{48}H_{66}$
Formula weight	1801.7
Space group	$P\bar{1}$
a (Å)	19.032(4)
b (Å)	13.328(2)
c (Å)	14.401(2)
α (°)	92.69(1)
β (°)	92.18(2)
γ (°)	108.01(3)
V (Å ³)	3464(2)
Z	2
D_{calc} (g/cm ³)	1.727
Crystal size (mm)	0.40 × 0.10 × 0.80
$\mu(K\alpha)$ (cm ⁻¹)	14.915 (Mo)
Data collection instrument	Syntex P3/F
Radiation monochromated (Å)	Mo $K\alpha$, 0.71073
Orientation reflections: no., range	25, $22 \leq 2\theta \leq 32$
Temperature (°C)	21 (± 2)
Scan method	ω - 2θ
Data collection range, 2θ (°)	$4 \leq 2\theta \leq 46$
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	7337, 5754
No. parameters refined	649
Transmission factors: max., min.	0.999, 0.810
R^a	0.0614
R_w^b	0.0757
Quality-of-fit indicator ^c	1.486
Largest shift/e.s.d., final cycle	0.07
Largest peak (e/Å ³)	1.652

$$^a R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$^b R_w = \frac{[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}}{w = 1/\sigma^2(|F_o|)}$$

$$^c \text{Quality-of-fit} = \frac{[\sum w(|F_o| - |F_c|)^2 / (N_{obs} - N_{param})]^{1/2}}$$

Table 2
Average bond distances (Å) and angles (°)^a

Zr–Zr	3.230[17]
Zr–Cl	2.572[8]
Zr–P	2.810[10]
Zr–Cl–Zr	77.8[4]
Cl–Zr–Cl(<i>cis</i>)	89.4[7]
Cl–Zr–Cl(<i>trans</i>)	167.8[4]

^aThe numbers in square brackets are mean deviations from the arithmetic means of all values that would be equal if both molecules had full octahedral symmetry within the $Zr_6Cl_{12}P_6$ core.

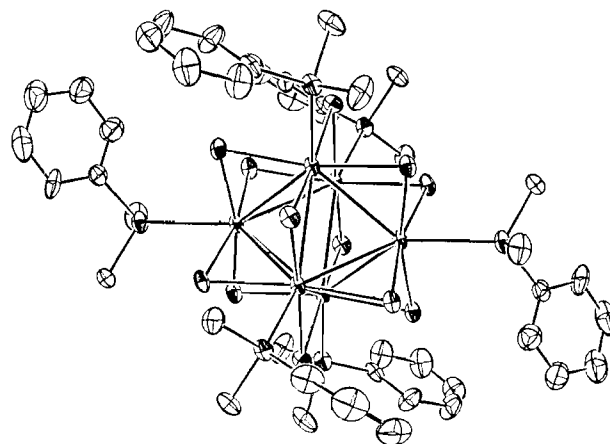


Fig. 1. A drawing of one of the two independent molecules in the unit cell. The other is virtually identical.

2.3. Other physical measurements

The magnetic susceptibility was measured over the temperature range 5–298 K by Dr S. Martin in the laboratory of Professor J.D. Corbett at Iowa State University. It showed only a 7% variation over this entire range and the mean value, corrected for inherent diamagnetism was 4.50×10^{-3} emu/mole. In view of this, attempts to record ³¹P NMR or ¹H NMR spectra were not made, since the $Zr_6Cl_{14}(PR_3)_4$ compounds, which also show TIP, gave only broad, poorly resolved signals.

3. Discussion

The problem of reproducibly preparing this compound in useful (though still relatively small) yields has been solved. The preparative procedure begins in the same way as that for the recently reported $Zr_6Cl_{14}(PMe_3)_4$ compounds [3] and presumably generates $Zr_6Cl_{14}(PMe_2Ph)_4$ as an intermediate. In order to effect further reduction, two molar equivalents of the stronger reducing agent Na/Hg are then employed.

The crystalline material that we have now obtained is a polymorph of that previously reported. The space group is $P\bar{1}$ with $Z = 2$, but contrary to the common

situation, there are two crystallographically distinct molecules, each residing on an inversion center. The number of independent distances and angles of each type is so large that we do not report them here individually. Instead, Table 2 gives the mean values and their variances. There are no significant differences between these mean values and those found previously in the other polymorph. For example, the previous mean Zr–Zr distance was 3.223[3] Å, compared to 3.230[17] found here. The only significant differences between the three molecules that have now been independently characterized structurally lies in small changes in the rotational orientations of the PMe_2Ph ligands about the Zr–P bond axes.

The final electron density difference map, as for the other polymorph, is devoid of any significant electron density within the Zr_6 clusters. Clearly, there could not be any atom at the center larger than a hydrogen atom.

The question of whether any hydrogen atoms are present in the $\text{Zr}_6\text{Cl}_{12}(\text{PMe}_2\text{Ph})_6$ compound, and if so, how many remains open, but we are now inclined to give that possibility serious consideration. In a recent report [4] on $\text{Zr}_5\text{X}_{12}(\text{PR}_3)_5\text{H}_4$ compounds, we offer direct evidence for the presence of the hydrogen atoms, and there is significant, though no conclusive evidence that several hydrogen atoms may be present in ' $\text{Zr}_6\text{Cl}_{14}(\text{PR}_3)_4$ ', ' $\text{Zr}_6\text{Cl}_{18}^{3-}$ ' and ' $\text{Zr}_6\text{Cl}_{18}^{4-}$ ' species [5].

It should be noted that all Zr_6 and Zr_5 species have so far been obtained in reasonable yield only when the hydridic reducing agent $(\text{C}_4\text{H}_9)_3\text{SnH}$ is employed. The extremely poor yields and lack of reproducibility in the original preparation of $\text{Zr}_6\text{Cl}_{12}(\text{PMe}_2\text{Ph})_6$ may be due to the dependence of that route on an adventitious source of hydrogen atoms.

As yet there is no evidence to positively suggest the presence of hydrogen atoms, but at the same time there are no data that could rule it out. The fact that the compound has a substantial temperature-independent paramagnetism makes it impossible to obtain NMR evidence.

Because there is no normal, temperature-dependent magnetic behavior, nor any detectable EPR spectrum, the number of hydrogen atoms would have to be even, and most likely, there would be two. This would bring the number of cluster based electrons to 14, the number

most favored in the centered Zr_6 clusters of Ziebarth and Corbett [2]. If there are, in fact, two hydrogen atoms, they would most likely reside in or just outside of two opposite triangular faces of the Zr_6 octahedron¹.

The fact that in neither of the crystal structures of the two polymorphs is there any sign of hydrogen atoms is also inconclusive. Taking the two polymorphic forms, there are altogether three $\text{Zr}_6\text{Cl}_{12}(\text{PMe}_2\text{Ph})_6$ molecules whose structures have been independently determined. In none of them can any subset of faces be found that are significantly larger or smaller than the others. Thus, if there are two faces capped with hydrogen atoms, they must in all three cases be randomly disordered over four orientations. This makes it impossible to detect the presence of the hydrogen atoms since there would be, effectively, only one quarter of an H atom at each position in the crystal.

4. Supplementary material

Non-hydrogen fractional atomic coordinates and equivalent isotropic thermal parameters are available from author F.A.C. on request.

Acknowledgement

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¹Molecular orbital calculations were made by Dr Xuejun Feng for a $\text{Zr}_6\text{Cl}_{12}(\text{PR}_3)_6\text{H}_2$ molecule with the H atoms centered at 0.1 Å above each of two opposite Zr_3 faces, so as to give the $\text{Zr}_6\text{Cl}_{12}\text{P}_6\text{H}_2$ skeleton D_{3h} symmetry. A closed shell structure with 14 core electrons is thereby predicted.