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Pentanuclear Zirconium Clusters with Chloride, Hydride, and Phosphine Ligands

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Abstract: The synthesis and characterization of new zirconium cluster compounds of composition $H_4Zr_5Cl_{12}(PR_3)_5$ are reported. By reaction of $ZrCl_4$ with 1.60 mol equiv of Bu_3SnH followed by 1 mol equiv of PR_3, the pentanuclear species are obtained rather than the previously described hexanuclear ones, $Zr_6Cl_{14}(PR_3)_4$. The compounds with $PR_3 = PMe_3$ (**1**), PEt_3 (**2**), and PMe_2Ph (**3**) have been characterized by X-ray crystallography and by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. Compound **1**$\cdot C_6H_6$ crystallizes in the triclinic space group $P\bar{1}$ with cell dimensions (−100 °C) of a = 11.833(2) Å, b = 12.001(1) Å, c = 20.167(2) Å, α = 77.651(9)°, β = 86.627(9)°, γ = 64.23(1)°, V = 2517.4(5) Å^3, and Z = 2. Compound **2** crystallizes in the monoclinic space group $C2/c$ with cell dimensions (−75 °C) of a = 48.06(1) Å, b = 12.667(2) Å, c = 22.829(5) Å, β = 113.36(2)°, V = 12 758(11) Å^3, and Z = 8. Compound **3** crystallizes in the triclinic space group $P\bar{1}$ with cell dimensions (21 °C) of a = 12.623(2) Å, b = 13.715(3) Å, c = 19.382(4) Å, α = 91.58(2)°, β = 96.78(2)°, γ = 116.20(1)°, V = 2978(2) Å^3, and Z = 2. These diamagnetic compounds have NMR spectra showing that they retain solution structures that are similar to those in the crystals. Furthermore, the ^1H NMR spectra of **2** and **3** show resonances at −1.18 and −2.58 ppm, respectively, which integrate to four hydride ligands per Zr_5 cluster. In all cases, the Zr atoms define a distorted pyramid with a rectangular base. There are two long basal edges (3.41–3.54 Å) and two short ones (3.20–3.31 Å). The slant edges are similar in length (3.29–3.33 Å) to the short basal edges. All eight of the Zr–Zr edges are bridged by a μ-Cl atom. One PR_3 ligand is bonded above the apical zirconium atom, and the others are bonded to the basal zirconium atoms, with two opposite ones in the basal plane and the other two below it. By using X-ray data collected at −100 °C, the four hydride ligands were found in (**1**$\cdot C_6H_6$), two just inside the centers of the triangular Zr_3 faces with the longer basal edges [$Zr{-}\mu_3{-}H$ = 1.96(3) Å] and two symmetrically placed below the short basal edges [$Zr{-}\mu_2{-}H$ = 1.96(8) Å]. All four of these crystallographically independent hydrogen atoms refined well.

Introduction

Zirconium has a marked tendency to form cluster species in which edge-bridging halogen atoms are always present.[1,2] Among the ones already known, a major class comprises those that are hexanuclear and octahedral in shape.[3] In those studied extensively by the Corbett group, all of which are made by typical high-temperature solid-state methods, an atom of either a nonmetal (Be, B, C, N)[4] or a metal (Fe, Co, Ni)[5] occupies the center of the cluster, whereas, in octahedral species previously reported from this laboratory[6] and synthesized under mild conditions (room temperature in arene solvents), it is clear that no atom heavier than H could be present inside the cluster. Without necessarily ruling out the possibility that one or more hydrogen atoms might be present on (or in) the Zr_6 octahedron, we have referred to these, for which typical formulas are $Zr_6Cl_{12}(PR_3)_6$ and $Zr_6Cl_{14}(PR_3)_4$, as "empty" clusters.[6] It is, of course known that there are hexazirconium[7a–d] and hexathorium[7e,f] clusters which contain one or more hydrogen atoms.

We now report that under vary mild conditions, quite similar to those that afford "empty" octahedral clusters, we have synthesized compounds that contain five zirconium atoms arranged to form a distorted pyramid with a roughly rectangular base. Apart from hydrogen atoms, these compounds all have composition $Zr_5Cl_{12}(PR_3)_5$. The only inorganic cluster compound that we are aware of with an approximately similar metal core geometry is the anion in $[NBu_4]_2[Mo_5Cl_{13}]$.[8] Some organometallic carbido and nitrido clusters with carbonyl ligands, $M_5(CO)_{15}C$ (M = Fe,[9] Ru,[10] Os[11]) and $[Fe_5(CO)_{14}N]^-$,[12] have also been described. The three $H_4Zr_5Cl_{12}(PR_3)_5$ compounds, with $PR_3 = PMe_3$ (**1**), PEt_3 (**2**), and PMe_2Ph (**3**), that we report here have been characterized by X-ray crystallography and by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy.

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Experimental Section

All manipulations were conducted under an argon atmosphere by using standard vacuum line and Schlenk techniques. Glassware was oven dried at 150 °C for 24 h prior to use. Solvents were predried over molecular sieves and freshly distilled under nitrogen from appropriate drying reagents. $ZrCl_4$, $HSn(n\text{-}Bu)_3$ (d_{20} = 1.103 g/mL), and phosphines were purchased from Strem Chemicals and used as received. The $^{31}P\{^1H\}$ and ^1H NMR spectra were collected on a Varian XL-200 spectrometer.

Preparation of $(\mu_2\text{-}H)_2(\mu_3\text{-}H)_2Zr_5Cl_{12}(PMe_3)_5{\cdot}C_6H_6$ ($\mathbf{1}{\cdot}C_6H_6$), $H_4Zr_5Cl_{12}(PEt_3)_5$ (2), and $H_4Zr_5Cl_{12}(PMe_2Ph)_5$ (3). $ZrCl_4$ (0.466 g, 2.0 mol) was placed in a 100-mL flask equipped with a stirring bar, and 20 mL of benzene was added by syringe. The $ZrCl_4/C_6H_6$ mixture was vigorously stirred as $(n\text{-}C_4H_9)_3SnH$ (0.85 mL, 3.2 mmol) was added dropwise by syringe. The addition of the $(n\text{-}C_4H_9)_3SnH$ caused effervescence, presumably from formation of H_2 gas, and the appearance of a brown precipitate over a 12-h period. This reaction mixture was stirred for a total of 24 h, after which the orange-yellow supernatant liquid was decanted. The brown precipitate was washed with 20 mL of fresh benzene solvent, followed by addition of 20 mL of fresh benzene solvent for **1** or toluene for **2** and **3**. One equivalent of phosphine (PMe_3, 0.20 mL, 2.0 mmol; PEt_3, 0.30 mL, 2.0 mmol; PMe_2Ph, 0.28 mL, 2.0 mmol) was added by syringe, producing a dark-brown solution, which was filtered into a 50-mL Schlenk tube and layered with 30 mL of hexanes. The $H_4Zr_5Cl_{12}(PR_3)_5$ solutions were extremely sensitive to air and moisture and decomposed to white flocculent precipitates upon short-term exposure (<5 s) to the atmosphere.

Dark-brown crystals of $\mathbf{1}{\cdot}C_6H_6$ and **3** appeared in 2 weeks. Irregular shaped crystals of **2** were obtained after placing the fully diffused hexane/toluene solution in a freezer (–20 °C) for 3 weeks. The isolated crystalline yields of $\mathbf{1}{\cdot}C_6H_6$, **2**, and **3**, were 117 mg (21.8%), 97 mg (16.5%), and 153 mg (24%), respectively. $^{31}P\{^1H\}$ NMR (C_6H_6/C_6D_6, 23 °C, 81 MHz): **2** δ = –18.8 (br s, free PEt_3), –4.6 (s, 1 P), –1.3 (s, 2 P), –0.5 (s, 2 P); **3** δ = –46.2 (br s, Free PMe_2Ph), –20.3 (s, 1 P), –18.1 (s, 2 P), –14.6 (s, 2 P). ^1H NMR (C_6D_6, 23 °C, 200 MHz): **2** δ = 2.18 (m, P–CH_2 (basal), 12 H), 1.85 (m, P–CH_2 (basal), 12 H), 0.7–1.4 (overlapping ms, P–CH_2 (apical) and –CH_3 (basal and apical)), –1.18 (br s, H(Zr), 4 H); **3** δ = 6.8–7.6 (overlapping ms, H_m phenyl), 1.93 (d, P–CH_3 (basal), 12 H, $^2J_{H-P}$ = 8 Hz), 1.58 (d, P–CH_3 (basal), 12 H, $^2J_{H-P}$ = 8 Hz), 1.02 (d, P–CH_3 (apical), 6 H, $^2J_{H-P}$ = 6 Hz), –2.58 (br s, H(Zr), 4 H). Attempts to obtain NMR spectra for **1** were unsuccessful because of its low solubility and sensitivity to oxygen and moisture.

X-ray Crystallography of $(\mu_2\text{-}H)_2(\mu_3\text{-}H)_2Zr_5Cl_{12}(PMe_3)_5{\cdot}C_6H_6$ ($\mathbf{1}{\cdot}C_6H_6$). Crystals were examined in a stream of nitrogen under a mixture of mineral oil and mother liquor (4:1), coated with Apiezon-T stopcock grease, mounted on the tip of a quartz fiber, and placed in a cold stream of nitrogen (–100 °C) on an Enraf-Nonius CAD-4 diffractometer. Cell parameters were obtained by centering and indexing 17 reflections found from a semiautomatic search routine, refined by centering 25 reflections in the range 35° < 2θ < 37°, and confirmed by axial photography.

The intensity data were gathered by the ω–2θ scan method. Equivalent data were monitored in the range 4° < 2θ < 25°; only unique data were collected for 25° < 2θ < 50°. During the data collection three orientation and three intensity reflections were monitored after every 250 reflections and 2 h, respectively.

The intensity data were corrected for Lorentz and polarization effects.[13a] An empirical absorption correction based on azimuthal scans of seven reflections with their χ-angle near 90° was applied;[13b] no correction for decay was necessary. The R_{int} for averaging of 2830 equivalent data was 0.011. The possible space groups were $P1$ and $P\bar{1}$. Successful refinement of the structure confirmed the latter. The initial coordinates of the Zr, Cl, and P atoms were provided by direct methods.[13c] The structure refinement was conducted with the SHELXL-93 software package[13d,e] employing all data and full matrix least-squares refinement on F^2. After the heavy atoms had been refined anisotropically, it became apparent that the methyl carbon atoms associated with P(1) and P(3) were disordered over four and three sites, respectively. The disordered models of the PMe_3 ligands were refined by constraining key interatomic distances (i.e., P–C, 1.87 Å; C···C, 3.08 Å) and refining the site occupancy factors for the different orientations of carbon atoms on each phosphorus atom so that they totaled 1. The occupancy values converged to the following values: 0.254(16), C(10A)–C(12A); 0.103(13), C(10B)–C(12B); 0.211(12), C(10C)–C(12C); 0.436(17), C(10D)–C(12D); 0.543(27), C(30A)–C(32A); 0.352(26), C(30B)–C(32B); 0.108(18), C(30C)–C(32C). After refinement of this disorder model, the hydrogen atoms appeared in the difference Fourier map. The hydrogen atoms on the Zr_5 core were the first to appear with peak heights in the range 1.3–1.5 $e^-/Å^3$. All other hydrogen atoms, except those associated with the disordered PMe_3 ligands and benzene solvent molecule, were found and refined. The final difference map was featureless with the highest peak of 0.9 $e^-/Å^3$ only 1 Å from P(1). Additional crystallographic data are presented in Table 1. Selected bond distances and angles are listed in Table 2.

Table 1. Crystal Data for $(\mu_2\text{-}H)_2(\mu_3\text{-}H)_2Zr_5Cl_{12}(PMe_3)_5{\cdot}C_6H_6$ ($\mathbf{1}{\cdot}C_6H_6$), $H_4Zr_5Cl_{12}(PEt_3)_5$ (**2**), and $H_4Zr_5Cl_{12}(PMe_2Ph)_5$ (**3**)

	$\mathbf{1}{\cdot}C_6H_6$	**2**	**3**
formula	$Zr_5Cl_{12}P_5C_{21}H_{51}$	$Zr_5Cl_{12}P_5C_{30}H_{75}$	$Zr_5Cl_{12}P_5C_{40}H_{55}$
formula weight	1340.0	1472.3	1572.3
space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
a, Å	11.833(2)	48.06(1)	12.623(2)
b, Å	12.001(1)	12.667(2)	13.715(3)
c, Å	20.167(2)	22.829(5)	19.382(4)
α, deg	77.651(9)	90.00	91.58(2)
β, deg	86.627(9)	113.36(2)	96.78(2)
γ, deg	64.23(1)	90.00	116.20(1)
V, Å^3	2517.4(5)	12758(11)	2978(2)
Z	2	8	2
d_{calc}, g/cm^3	1.768	1.533	1.753
μ(Mo Kα), cm^{-1}	18.12	14.303	15.382
temp, °C	–100(2)	–75(2)	21(2)
transmission factors, max, min	0.9996, 0.8494	0.9992, 0.7420	0.9967, 0.6041
R	0.034 (all data)[a]	0.076[a]	0.043[a]
R_w (wR^2)	(0.078, all data)[b,c]	0.122[d,e]	0.055[d,e]
quality(goodness)-of-fit indicator[c]	(1.086)[f,c]	2.696[g,e]	1.022[g,e]

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR^2 = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$. [c] $w = [\sigma^2(F_o^2) + (0.0318(\max(F_o^2,0) + 2F_c^2)/3)^2 + 4.938(\max(F_o^2,0) + 2F_c^2)/3]^{-1}$. [d] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [e] $w = 1/\sigma^2(|F_o|)$. [f] Goodness-of-fit = $[\sum w(|F_o^2| - |F_c^2|)^2/(N_{obs} - N_{parameters})]^{1/2}$. [g] Quality-of-fit = $[\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

X-ray Crystallography of $H_4Zr_5Cl_{12}(PEt_3)_5$ (2). A dark-brown crystal was mounted on the tip of a quartz fiber and placed in a cold stream of nitrogen (–75 °C) on an Enraf-Nonius CAD-4 diffractometer. The unit cell was indexed on 20 strong reflections in the range 29° < 2θ < 34° that were located by a semiautomatic search routine. A monoclinic C-centered cell was obtained. The C-centering, Laue class, and lattice dimensions were confirmed by oscillation photography. Intensity data were collected by the ω-scan method in the range 4° < 2θ < 46°.

The intensity data were corrected for Lorentz and polarization effects and for anisotropic decay, and an empirical absorption correction based on seven ψ-scans was also applied.[13a,b] The R_{int} for averaging equivalent data was 0.038. Systematic absences narrowed the space group choices to $C2/c$ and Cc. The structure was solved in $C2/c$ by direct methods.[13c] The Zr, Cl, and P atoms refined routinely. The carbon atoms were located by iterative application of least-squares analysis and difference Fourier maps.[13a] A two-fold disorder of the β-carbon atoms of some of PEt_3 ligands was found at this stage of the refinement. Since electron densities for each pair of positions, C(24a,b), C(33a,b), C(34a,b), and C(35a,b), on a difference Fourier map were close, in the final refinement all such sites were assigned site occupancy values of 0.5, and the atoms of each pair were given a common thermal parameter. Bond and interatomic distance constraints C(α)–C(β), C(β)–C(β), and P–C(β) were also applied to the disordered PEt_3 ligands. The hydrogen atoms on the Zr_5 core of this compound could not be located during the structure refinement. The final difference Fourier map had a few peaks with height of 1.5 $e^-/Å^3$ near the zirconium atoms (<1 Å). The refinement of the structure in space group Cc resulted in chemically unreasonable molecular dimensions and thermal parameters. Crystal data are compiled in Table 1. Selected bond distances and angles are listed in Table 3.

X-ray Crystallography of $H_4Zr_5Cl_{12}(PMe_2Ph)_5$ (3). A thin brown crystal with dimensions of 0.35 × 0.05 × 0.40 mm^3 was wedged into a

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Table 2. Selected Listing of Bond Lengths (Å) and Angles (deg) for $(\mu_2\text{-H})_2(\mu_3\text{-H})_2Zr_5Cl_{12}(PMe_3)_5{\cdot}C_6H_6$ ($\mathbf{1}{\cdot}C_6H_6$)[a]

Bond Distances

Zr(1)–Zr(2)	3.5388(7)	Zr(4)–Zr(5)	3.3113(6)
Zr(1)–Zr(4)	3.2136(6)	Zr(4)–Cl(4)	2.5624(9)
Zr(1)–Zr(5)	3.2996(6)	Zr(4)–Cl(7)	2.5671(11)
Zr(1)–Cl(1)	2.5992(9)	Zr(4)–Cl(8)	2.5376(10)
Zr(1)–Cl(5)	2.5989(10)	Zr(4)–Cl(12)	2.5162(9)
Zr(1)–Cl(8)	2.5501(10)	Zr(4)–P(4)	2.7512(10)
Zr(1)–Cl(9)	2.4397(9)	Zr(5)–Cl(1)	2.5554(10)
Zr(1)–P(1)	2.7718(12)	Zr(5)–Cl(2)	2.5479(9)
Zr(2)–Zr(3)	3.2026(6)	Zr(5)–Cl(3)	2.5556(10)
Zr(2)–Zr(5)	3.3153(6)	Zr(5)–Cl(4)	2.5382(9)
Zr(2)–Cl(2)	2.5714(9)	Zr(5)–P(5)	2.7770(10)
Zr(2)–Cl(5)	2.5610(10)	Zr(1)–H(1)	2.00(4)
Zr(2)–Cl(6)	2.5379(10)	Zr(1)–H(4)	2.07(4)
Zr(2)–Cl(10)	2.5186(9)	Zr(2)–H(1)	1.96(4)
Zr(2)–P(2)	2.7497(10)	Zr(2)–H(3)	1.90(4)
Zr(3)–Zr(4)	3.5403(7)	Zr(3)–H(2)	1.99(4)
Zr(3)–Zr(5)	3.2993(7)	Zr(3)–H(3)	1.96(4)
Zr(3)–Cl(3)	2.5816(10)	Zr(4)–H(2)	1.97(4)
Zr(3)–Cl(6)	2.5546(10)	Zr(4)–H(4)	1.89(4)
Zr(3)–Cl(7)	2.5998(10)	Zr(5)–H(1)	1.93(4)
Zr(3)–Cl(11)	2.4627(10)	Zr(5)–H(2)	1.93(4)
Zr(3)–P(3)	2.7724(12)		

Bond Angles

Zr(4)–Zr(1)–Zr(5)	61.098(12)	Zr(3)–Zr(5)–Zr(4)	64.76(2)
Zr(4)–Zr(1)–Zr(2)	95.14(2)	Zr(1)–Zr(5)–Zr(4)	58.170(12)
Zr(5)–Zr(1)–Zr(2)	57.873(12)	Zr(3)–Zr(5)–Zr(2)	57.915(13)
Zr(3)–Zr(2)–Zr(5)	60.793(14)	Zr(1)–Zr(5)–Zr(2)	64.684(13)
Zr(3)–Zr(2)–Zr(1)	84.39(2)	Zr(4)–Zr(5)–Zr(2)	97.674(14)
Zr(5)–Zr(2)–Zr(1)	57.443(12)	Zr(5)–Cl(1)–Zr(1)	79.60(3)
Zr(2)–Zr(3)–Zr(5)	61.292(13)	Zr(5)–Cl(2)–Zr(2)	80.72(3)
Zr(2)–Zr(3)–Zr(4)	95.31(2)	Zr(5)–Cl(3)–Zr(3)	79.92(3)
Zr(5)–Zr(3)–Zr(4)	57.784(14)	Zr(5)–Cl(4)–Zr(4)	80.96(3)
Zr(1)–Zr(4)–Zr(5)	60.732(12)	Zr(2)–Cl(5)–Zr(1)	86.60(3)
Zr(1)–Zr(4)–Zr(3)	84.21(2)	Zr(2)–Cl(6)–Zr(3)	77.93(3)
Zr(5)–Zr(4)–Zr(3)	57.455(13)	Zr(4)–Cl(7)–Zr(3)	86.50(3)
Zr(3)–Zr(5)–Zr(1)	86.82(2)	Zr(4)–Cl(8)–Zr(1)	78.34(3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 3. Selected Listing of Bond Distances (Å) and Angles (deg) for $H_4Zr_5Cl_{12}(PEt_3)_5$ (**2**)[a]

Bond Distances

Zr(1)–Zr(2)	3.506(2)	Zr(3)–Cl(3)	2.579(3)
Zr(1)–Zr(4)	3.288(2)	Zr(3)–Cl(6)	2.575(5)
Zr(1)–Zr(5)	3.300(2)	Zr(3)–Cl(7)	2.583(4)
Zr(1)–Cl(1)	2.580(3)	Zr(3)–Cl(11)	2.452(4)
Zr(1)–Cl(5)	2.585(4)	Zr(3)–P(3)	2.804(6)
Zr(1)–Cl(8)	2.563(4)	Zr(4)–Zr(5)	3.327(2)
Zr(1)–Cl(9)	2.447(4)	Zr(4)–Cl(4)	2.577(3)
Zr(1)–P(1)	2.799(5)	Zr(4)–Cl(7)	2.552(6)
Zr(2)–Zr(3)	3.301(2)	Zr(4)–Cl(8)	2.552(5)
Zr(2)–Zr(5)	3.325(2)	Zr(4)–Cl(12)	2.503(4)
Zr(2)–Cl(2)	2.543(3)	Zr(4)–P(4)	2.794(4)
Zr(2)–Cl(5)	2.560(5)	Zr(5)–Cl(1)	2.549(4)
Zr(2)–Cl(6)	2.553(6)	Zr(5)–Cl(2)	2.531(3)
Zr(2)–Cl(10)	2.501(4)	Zr(5)–Cl(3)	2.542(5)
Zr(2)–P(2)	2.797(4)	Zr(5)–Cl(4)	2.542(3)
Zr(3)–Zr(4)	3.503(2)	Zr(5)–P(5)	2.804(3)
Zr(3)–Zr(5)	3.298(2)		

Bond Angles

Zr(2)–Zr(1)–Zr(4)	94.10(5)	Zr(1)–Zr(5)–Zr(3)	89.12(5)
Zr(2)–Zr(1)–Zr(5)	58.40(4)	Zr(1)–Zr(5)–Zr(4)	59.49(4)
Zr(4)–Zr(1)–Zr(5)	60.67(4)	Zr(2)–Zr(5)–Zr(3)	59.77(4)
Zr(1)–Zr(2)–Zr(3)	85.66(5)	Zr(2)–Zr(5)–Zr(4)	96.80(4)
Zr(1)–Zr(2)–Zr(5)	57.70(4)	Zr(3)–Zr(5)–Zr(4)	63.83(4)
Zr(3)–Zr(2)–Zr(5)	59.71(4)	Zr(1)–Cl(1)–Zr(5)	80.1(1)
Zr(2)–Zr(3)–Zr(4)	93.94(5)	Zr(2)–Cl(2)–Zr(5)	81.9(1)
Zr(2)–Zr(3)–Zr(5)	60.52(4)	Zr(3)–Cl(3)–Zr(5)	80.2(1)
Zr(4)–Zr(3)–Zr(5)	58.49(4)	Zr(4)–Cl(4)–Zr(5)	81.08(9)
Zr(1)–Zr(4)–Zr(3)	85.90(4)	Zr(1)–Cl(5)–Zr(2)	85.9(1)
Zr(1)–Zr(4)–Zr(5)	59.84(4)	Zr(2)–Cl(6)–Zr(3)	80.1(2)
Zr(3)–Zr(4)–Zr(5)	57.68(4)	Zr(3)–Cl(7)–Zr(4)	86.0(2)
Zr(1)–Zr(5)–Zr(2)	63.90(4)	Zr(1)–Cl(8)–Zr(4)	80.0(1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Lindemann capillary tube that had been previously filled with dried and degassed mineral oil. The tube was sealed at both ends with epoxy cement and placed on the goniometer head of a Syntex P3/F diffractometer. For 14 reflections the X and Y coordinates were obtained from a rotation photograph and used to center the reflections. The unit cell was indexed and found to be triclinic. The cell parameters and orientation matrix were refined by centering 25 reflections in the range $21° < 2\theta < 28°$. Three intensity standards were gathered after every 97 intensity measurements, which showed no change in crystal orientation but an overall 17.1% decrease in intensity during the data collection.

Lorentz, polarization, decay, and empirical absorption corrections were applied to the data.[13a,b] The R_{int} for averaging of equivalent data was 0.034.

The initial coordinates of the Zr, Cl, and P atoms were obtained by direct methods.[13c] The other non-hydrogen atoms were located in a routine fashion by alternating sequences of least-squares refinements and difference Fourier maps. All non-hydrogen atoms were then refined anisotropically to convergence. It was not possible to locate the hydrogen atoms from the difference Fourier maps for this structure. Additional crystal data are compiled in Table 1. Selected bond distances and angles are listed in Table 4.

Results and Discussion

Synthesis. The $H_4Zr_5Cl_{12}(PR_3)_5$ clusters were prepared by a method similar to that employed for hexazirconium compounds of composition $Zr_6X_{14}(PR_3)_4$ (X = Cl or Br; R = Me, Et, *n*-Pr),[6] namely reduction of $ZrCl_4$ with tri(*n*-butyl)tin hydride followed by addition of phosphine ligands. The smaller amount of tri-*n*-butyltin hydride used in the synthesis of the Zr_5 clusters (1.6 equiv), as compared to that used for the Zr_6 clusters (1.66 equiv), appears to be the critical factor in their formation over the Zr_6 clusters. Interestingly, in some M_5/M_6 cluster systems, for example $Ru_5(CO)_{15}C/Ru_6(CO)_{18}C$[10] and $[Mo_5Cl_{13}]^{2-}/[Mo_6Cl_{14}]^{2-}$,[8] either the M_5 cluster is made from the M_6 cluster, as in the Ru_5/Ru_6 system, or both cluster types form under similar reaction conditions, as found for the Mo_5/Mo_6 system. We have not yet determined the relationship, if any, between the processes leading to the $H_4Zr_5Cl_{12}(PR_3)_5$ and Zr_6 cluster types. The presence of hydride ligand on the Zr_5 clusters not only is consistent with the use of a hydride reducing agent in the synthetic scheme but now raises the question of whether the Zr_6 clusters also contain hydride ligands.

Crystal Structure of $(\mu_2\text{-H})_2(\mu_3\text{-H})_2Zr_5Cl_{12}(PMe_3)_5{\cdot}C_6H_6$ ($\mathbf{1}{\cdot}C_6H_6$). The crystal structure consists of discrete Zr_5 clusters and interstitial benzene solvent, each residing on a general position in the triclinic unit cell.[14] An ORTEP drawing of compound **1** is shown in Figure 1. The cluster has a pyramidal arrangement of zirconium atoms with each of the eight edges bridged by chlorine atoms. The arrangement of the four basal phosphine ligands is relatively unsymmetrical; two of them project "horizontally" and two project down. The terminal chlorine atoms have a similar but complementary arrangement. On this basis the highest possible point symmetry (neglecting the organic groups on the phosphine ligands) of the $Zr_5Cl_{12}P_5$ core is C_{2v}. However, as can be seen from Figure 1 and the molecular dimensions listed in Table 2, the fact that the Zr_5 core has two long and two short basal edges lowers the highest possible symmetry to C_2. The lack of planarity in the base destroys even this remaining symmetry.

Three types of Zr–Zr bond distances are present in the structure, namely Zr_{basal}–Zr_{basal}(long), Zr_{basal}–Zr_{basal}(short), and Zr_{basal}–Zr_{apical}. The difference between the average "long" and "short" Zr_{basal}–Zr_{basal} bond distances is 0.33 Å. The average Zr_{basal}–

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(14) $H_4Zr_5Cl_{12}(PMe_3)_5$ also crystallizes in the monoclinic space group $P2_1/c$ with 1.5 C_6H_6 solvent molecules per formula unit: $a = 21.783(5)$ Å, $b = 12.092(3)$ Å, $c = 21.093(5)$ Å, $\beta = 101.74(2)°$, $V = 5{,}440(4)$ Å^3, $Z = 4$, $R = 0.0599$, $R_w = 0.0851$, quality-of-fit = 1.485 for 3863 reflections with $F_o^2 > 3\sigma(F_o^2)$. The molecular dimensions are essentially the same as those of **1**.

Table 4. Selected Listing of Bond Distances (Å) and Angles (deg) for $H_4Zr_5Cl_{12}(PMe_2Ph)_5$ (3)[a]

	Bond Distances		
Zr(1)–Zr(2)	3.423(1)	Zr(3)–Cl(3)	2.616(3)
Zr(1)–Zr(4)	3.305(2)	Zr(3)–Cl(6)	2.551(3)
Zr(1)–Zr(5)	3.285(2)	Zr(3)–Cl(7)	2.573(3)
Zr(1)–Cl(1)	2.591(4)	Zr(3)–Cl(11)	2.442(4)
Zr(1)–Cl(5)	2.583(4)	Zr(3)–P(3)	2.804(4)
Zr(1)–Cl(8)	2.565(3)	Zr(4)–Zr(5)	3.327(1)
Zr(1)–Cl(9)	2.452(4)	Zr(4)–Cl(4)	2.544(3)
Zr(1)–P(1)	2.797(4)	Zr(4)–Cl(7)	2.538(3)
Zr(2)–Zr(3)	3.300(2)	Zr(4)–Cl(8)	2.508(3)
Zr(2)–Zr(5)	3.320(2)	Zr(4)–Cl(12)	2.488(4)
Zr(2)–Cl(2)	2.550(4)	Zr(4)–P(4)	2.802(4)
Zr(2)–Cl(5)	2.542(3)	Zr(5)–Cl(1)	2.545(3)
Zr(2)–Cl(6)	2.534(3)	Zr(5)–Cl(2)	2.531(3)
Zr(2)–Cl(10)	2.485(3)	Zr(5)–Cl(3)	2.567(3)
Zr(2)–P(2)	2.773(4)	Zr(5)–Cl(4)	2.533(3)
Zr(3)–Zr(4)	3.407(2)	Zr(5)–P(5)	2.797(4)
Zr(3)–Zr(5)	3.301(2)		
	Bond Angles		
Zr(2)–Zr(1)–Zr(4)	98.46(4)	Zr(1)–Zr(5)–Zr(3)	82.02(4)
Zr(2)–Zr(1)–Zr(5)	59.27(3)	Zr(1)–Zr(5)–Zr(4)	59.97(3)
Zr(4)–Zr(1)–Zr(5)	60.64(3)	Zr(2)–Zr(5)–Zr(3)	59.80(4)
Zr(1)–Zr(2)–Zr(3)	79.97(4)	Zr(2)–Zr(5)–Zr(4)	100.12(4)
Zr(1)–Zr(2)–Zr(5)	58.29(3)	Zr(3)–Zr(5)–Zr(4)	61.87(3)
Zr(3)–Zr(2)–Zr(5)	59.81(4)	Zr(1)–Cl(1)–Zr(5)	79.5(1)
Zr(2)–Zr(3)–Zr(4)	98.87(4)	Zr(2)–Cl(2)–Zr(5)	81.59(9)
Zr(2)–Zr(3)–Zr(5)	60.38(4)	Zr(3)–Cl(3)–Zr(5)	79.11(9)
Zr(4)–Zr(3)–Zr(5)	59.44(3)	Zr(4)–Cl(4)–Zr(5)	81.9(1)
Zr(1)–Zr(4)–Zr(3)	80.15(4)	Zr(1)–Cl(5)–Zr(2)	83.8(1)
Zr(1)–Zr(4)–Zr(5)	59.39(3)	Zr(2)–Cl(6)–Zr(3)	80.94(9)
Zr(3)–Zr(4)–Zr(5)	58.69(3)	Zr(3)–Cl(7)–Zr(4)	83.6(1)
Zr(1)–Zr(5)–Zr(2)	62.44(4)	Zr(1)–Cl(8)–Zr(4)	81.30(9)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

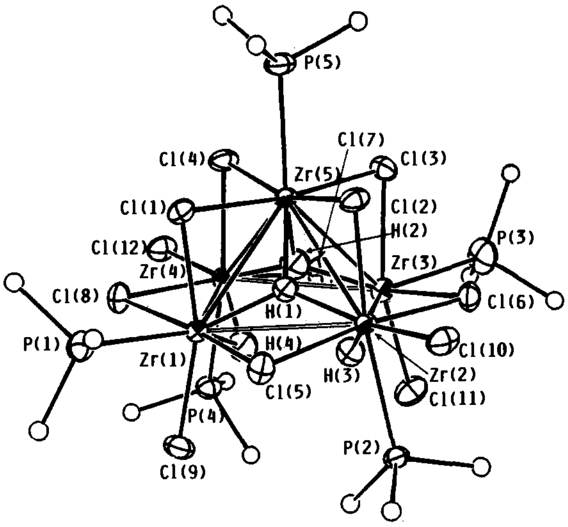

Figure 1. ORTEP drawing of the $(\mu_2\text{-H})_2(\mu_3\text{-H})_2\text{-}Zr_5Cl_{12}(PMe_3)_5$ molecule (1) showing the location of the four hydride ligands. Only one orientation of the disordered carbon atoms is shown. Carbon atoms have been given arbitrary thermal parameters for clarity; all other atoms are represented by their ellipsoids at the 50% probability level.

Zr_{basal}(short) and Zr_{basal}–Zr_{apical} bond distances differ by only 0.098 Å. Similarly, the average Zr_{basal}–Cl_{bridge}–Zr_{basal}(long) angle is 8.4° more obtuse than the average Zr_{basal}–Cl_{bridge}–Zr_{basal}(short) angle, whereas the Zr_{apical}–Cl_{bridge}–Zr_{basal} angle is only 2.2° more obtuse than the Zr_{basal}–Cl_{bridge}–Zr_{basal}(short) angle. Presumably, the Zr–Zr bonding strength is in the order Zr_{basal}–Zr_{basal}(short) > Zr_{basal}–Zr_{apical} > Zr_{basal}–Zr_{basal}(long).

The Zr–Cl_{bridge}, Zr–$Cl_{terminal}$, and Zr–P bond distances have the following ranges and average values: Zr–Cl_{bridge}, 2.538–2.599, 2.564(21) Å; Zr–$Cl_{terminal}$, 2.440–2.519, 2.484(39) Å; Zr–P 2.750–2.777, 2.764(13) Å. The Zr–$Cl_{terminal}$ and Zr–P bonds in the basal plane are 0.07 and 0.02 Å, respectively, longer than those below the basal plane. The difference in these bond lengths may be attributable to a combination of a trans influence from the H(3) and H(4) hydride ligands and greater ligand–ligand repulsions for the terminal ligands in the basal plane.

In addition to the distortion of the basal plane, from square to rectangular, it is also slightly twisted. Thus, the Zr(1) and Zr(3) atoms lie 0.11 Å below and the Zr(2) and Zr(4) atoms 0.11 Å above the least-squares mean plane for all four of them. The irregularity of the Zr_4 base can also be seen in the Zr–Zr–Zr(basal) angles which have a range of 84.39–95.31°. The Zr–Zr–Zr angles in the large and small Zr_3 faces have ranges of 57.92–61.29° and 57.44–64.76°, respectively. Thus, throughout the structure the angles deviate substantially from the ideal values of 90° and 60° for a square pyramid.

The four hydride ligands, two μ_3-H and two μ_2-H, of ($1{\cdot}C_6H_6$) were located crystallographically from an X-ray data set collected at –100 °C. The μ_3-hydride ligands are situated 0.16 Å inside the centers of the large Zr_3 triangular faces. The μ_2-hydride ligands bridge the short basal edges and reside 0.96 Å below the Zr_4 base. The presence of the hydride ligands at these sites is supported not only by direct location and refinement of the atoms but also by certain distortions in the $[Zr_5Cl_8]^{4+}$ core. For example, the bridging chlorine atoms on the long basal edges (i.e., Cl(5) and Cl(7)) lie an average of 0.27 Å *below* the Zr_4 base. The chlorine atoms on the short basal edges (i.e. Cl(6) and Cl(8)) lie 0.17 Å *above* the Zr_4 base. Presumably, these distortions occur to minimize the repulsions between the bridging chlorine atoms and the μ_2- and μ_3-hydride ligands.

The average Zr–(μ_3-H) and Zr–(μ_2-H) bond distances are 1.96(3) and 1.96(8) Å, respectively. The Zr–(μ_3-H)–Zr angles have a range of 114–127°, which is in accordance with the pyramidal bonding between the hydride ligand and the Zr_3 face. For comparison, the average Zr–(μ_2-H)–Zr angle is 110(3)°. The four hydride ligands have a distorted tetrahedral arrangement, as can be seen from the following values of the six H···H distances: H(1)···H(2), 1.95(3) Å; H(1)···H(3), 2.09(2) Å; H(1)···H(4), 2.41(2) Å; H(2)···H(3), 2.36(3) Å; H(2)···H(4), 2.06(2) Å; H(3)···H(4), 2.48(2) Å.

The Zr–H and H···H distances are similar to those reported for solid-state compounds of composition ZrBrD[15] and Zr_2Br_2D.[16] In the trigonal antiprismatic ZrBrD, the deuteride is located just inside (0.25 Å) the Zr_3 faces. The Zr–D bond distance and D···D contacts of 2.0273(6) and 2.204(8) Å, respectively, are slightly longer than those in ($1{\cdot}C_6H_6$). However, the molecular dimensions of ZrBrD were obtained from a neutron data set which typically gives longer M–H(D) bond distances than those obtained from X-ray data sets. The neutron-determined Zr–D bond distances in Zr_2Br_2D have a range of 2.031–2.200 Å. The D···D contact is 2.93(2) Å. The values of the H···H contacts in ($1{\cdot}C_6H_6$) and the D···D contacts in ZrBrD and Zr_2Br_2D are close to the sum of Van der Waals radii for an H-ligand (2.40 Å).[17] However, deviations from this value are expected, since H···H contact distances are, in part, dependent on their structural context.

Crystal Structure of $H_4Zr_5Cl_{12}(PEt_3)_5$ (2) and $H_4Zr_5Cl_{12}(PMe_2Ph)_5$ (3). Each cluster resides on a general position in its unit cell. ORTEP drawings of **2** and **3** are presented in Figures 2 and 3, respectively. The molecular dimensions of **2** are similar but not identical to those of **1**·C_6H_6. The mean difference in the long and short Zr_{basal}–Zr_{basal} bond distances is 0.21 Å. The average Zr_{basal}–Zr_{basal}(short) and Zr_{basal}–Zr_{apical} bond distances differ by only 0.02 Å. Concomitantly, the average Zr_{basal}–Cl_{bridge}–Zr_{basal}(long) angle is 5.9° more obtuse than the average Zr_{basal}–Cl_{bridge}–Zr_{basal}(short) angle, and the average Zr_{basal}–Cl_{bridge}–Zr_{apical} angle

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(15) Wijeyesekera, S. D.; Corbett, J. D. *Solid State Commun.* **1985**, *54*, 657.

(16) Wijeyesekera, S. D.; Corbett, J. D. *Inorg. Chem.* **1986**, *25*, 4709.

(17) Bond, A. *J. Phys. Chem.* **1964**, *68*, 441.

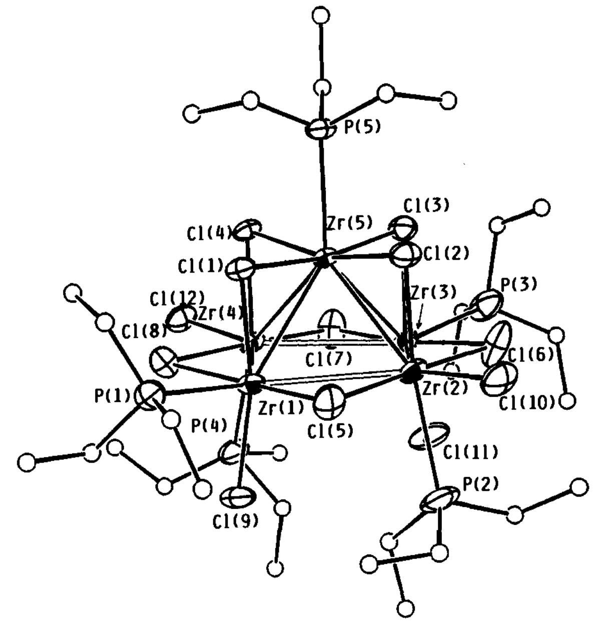

Figure 2. ORTEP drawing of the $H_4Zr_5Cl_{12}(PEt_3)_5$ molecule (2) with the atom-labeling scheme. Only one orientation of the disordered β-carbon atoms is shown. Carbon atoms have been given arbitrary thermal parameters for clarity; all other atoms are represented by their ellipsoids at the 50% probability level.

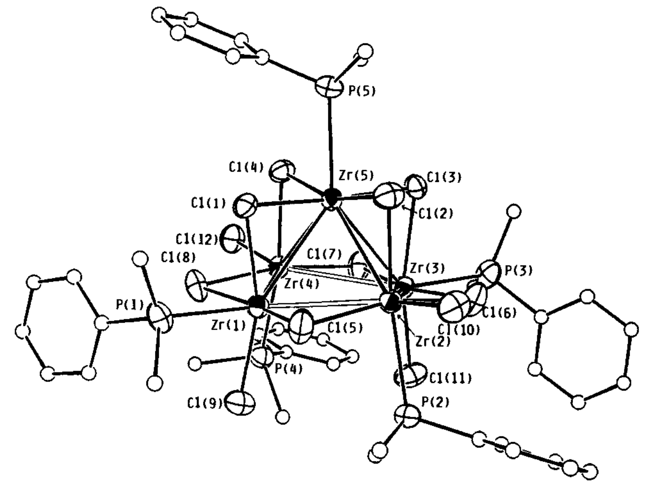

Figure 3. ORTEP drawing of the $H_4Zr_5Cl_{12}(PMe_2Ph)_5$ molecule (3). Carbon atoms have been given arbitrary thermal parameters for clarity; all other atoms are represented by their ellipsoids at the 50% probability level.

is only 0.75° more obtuse than the Zr_{basal}–Cl_{bridge}–Zr_{basal}(short) angle. The distortion of the Zr_5 core in 2 from a square pyramid is slightly less than that in $1{\cdot}C_6H_6$.

The Zr_4 base in 2 is, again, not strictly planar. Opposite pairs of Zr atoms lie 0.07 Å above or below the mean plane through Zr(1)–Zr(4). The Cl(5) and Cl(7), and Cl(6) and Cl(8) atoms are situated an average of 0.08 and 0.15 Å below and above, respectively, a least-squares plane through Zr(1)–Zr(4). Although the hydride ligands of 2 were not located crystallographically, there are structural distortions to suggest that they are present at the same sites as those on $1{\cdot}C_6H_6$.

The smallest difference in the long and short basal edges, only 0.11 Å, of a Zr_5 core is found in compound 3. On the other hand, as can be seen from the ORTEP drawing in Figure 3, the $[Zr_5Cl_8]^{4+}$ core of 3 is more twisted than that in either $1{\cdot}C_6H_6$ or 2. The four basal zirconium atoms reside an average of 0.18 Å, alternately up and down, from the mean plane through the Zr(1)-Zr(4) atoms. Similarly, the Cl(1) and Cl(3), and Cl(2) and Cl(4) atoms sit an average of 0.17 Å from a least-squares plane drawn through the Cl(1)–Cl(4) atoms. The Zr(5) atom lies 0.25 Å below this plane. The reason for the significant differences between the molecular dimensions of 3 and those of $1{\cdot}C_6H_6$ and 2 remains unclear. One contributing factor may be the tighter packing of molecules of 3 in the crystal. This is qualitatively supported by atomic volumes of the non-hydrogen atoms for 1, 2, and 3 of 29.3, 30.7, and 24.0 $Å^3$/atom, respectively.

$^{31}P\{^1H\}$ and ^1H NMR of $H_4Zr_5Cl_{12}(PEt_3)_5$ (2) and $H_4Zr_5Cl_{12}(PMe_2Ph)_5$ (3). The $^{31}P\{^1H\}$ NMR spectra of 2 and 3 contain three singlets corresponding to the three magnetically distinct phosphine ligands on the clusters: apical, basal (in plane), and basal (below plane). The $^3J_{P-P}$ couplings are apparently too small to be detected.

The ^1H NMR spectra of 2 and 3 provide additional evidence that hydride ligands are present on these clusters. In this respect, the salient features of the ^1H NMR spectra of 2 and 3 are the broad singlets at −1.18 and −2.58 ppm, respectively. These peaks integrate to four hydride ligands per Zr_5 cluster. The resonances for the hydrogen atoms of the PR_3 ligands were used as the reference for integration of the hydride resonances. The presence of only one broad peak in the upfield region of the ^1H NMR spectrum for each compound, even though two types of hydride ligands are present on the clusters (μ_2 and μ_3), indicates that these ligands are fluxional at room temperature. Low-temperature ^1H NMR studies are being undertaken in an attempt to confirm this.

The downfield region of the ^1H NMR spectrum of 2 is comprised of overlapping multiplets of methylene and methyl hydrogen atoms (P–CH_2, apical, and P–CH_2–CH_3, apical and basal) in the range 0.6–1.4 ppm. The methylene hydrogen atom resonances of the basal PEt_3 ligands occur as multiplets at 2.18 and 1.85 ppm. The downfield spectrum of 3 is comprised of overlapping phenyl hydrogen resonances in the range 6.8–7.6 ppm and three doublets between 1 and 2 ppm for the methyl hydrogen atoms on the three different types of PMe_2Ph ligands. The doublet splitting pattern arises from $^2J_{H-P}$ coupling. The doublets give the appropriate 12:12:6 integration.

Summary and Conclusions. (1) We report here the discovery of a class of compounds that are of an entirely new type for group 4 and almost without precedent in the transition block generally, namely, those with a cluster of five metal atoms in a rectangular pyramidal array. It is remarkable how sensitively the products of the preparative process, which is, broadly speaking, the same for both these new Zr_5 compounds and the previously reported Zr_6 compounds, depend on the precise quantity of the reducing agent, $(C_4H_9)_3SnH$, that is used. When ≥1.66 equiv per Zr is employed, the $Zr_6Cl_{14}(PR_3)_4$ species are obtained, in accord with the following stoichiometric relationship:

$$6Zr^{4+} + 6(1.66e^-) \rightarrow Zr_6^{14+} \qquad (1)$$

To obtain the Zr_5 species described here, we employed an appropriately smaller mole ratio of reducing agent, namely that which corresponds to the stoichiometric relationship

$$5Zr^{4+} + 5(1.60e^-) \rightarrow Zr_5^{12+} \qquad (2)$$

(2) We have obtained clear evidence that the new Zr_5 species contain four hydrogen atoms. This has been established by X-ray crystallography for 1 and confirmed for 2 and 3 by ^1H NMR.

(3) The presence of the H atoms in the $H_4Zr_5Cl_{12}(PR_3)_5$ compounds is consistent with the fact that the reducing agent used to prepare them is a potential hydride-transfer agent. It may be noted that the total reducing power of the $(C_4H_9)_3SnH$ used ($8e^-$ per Zr_5 cluster) is accompanied by more than the required number of H atoms to form the product.

Formally, eight H^- ions are used, four of which remain in the product cluster while the other four are (presumably) converted to $2H_2$. Whether one chooses to do the electron bookkeeping by regarding the product as four H atoms combined with Zr_5^{12+} or four H^- ions combined with Zr_5^{16+} is a purely formal matter of taste or convenience.

(4) Our finding that $(C_4H_9)_3SnH$ reacts with $ZrCl_4$ in part to transfer H^- ions and in part to transfer electrons clearly opens the question of whether it executes this dual role in the reactions leading to Zr_6 clusters. We now believe it to be very likely that it does so in at least some and possibly in all of those reactions. We have some direct evidence, as yet incomplete, that certain of the species previously formulated without hydrogen atoms[6] may actually contain them.[18] For example, we now believe that the previously described $Zr_6Cl_{14}(PR_3)_4$ molecules are $Zr_6Cl_{14}H_n(PR_3)_4$ molecules in which $n = 4$ or 5. We also have prepared "$[Zr_6Cl_{18}]^{n-}$" species that probably contain four H atoms.

(5) The placement of the four hydrogen atoms in the $H_4Zr_5Cl_{12}(PMe_3)_5$ molecule is suggestive of how four hydrogen atoms might be distributed in an octahedral $[Zr_6X_{12}H_4]L_6$ species, namely, at four alternating Zr_3 faces whereby a tetrahedral H_4 unit would be defined. If one more Zr atoms were to be added to the H_4Zr_5 cluster and the necessary adjustments made so that the six Zr atoms would define a regular octahedron, the four H atoms would require little or no changes in position to form such a tetrahedral array, mapped onto the Zr_6 octahedron.

Acknowledgment. We thank The Robert A. Welch Foundation for support under Grant A-494.

Supplementary Material Available: Tables of crystallographic data, bond lengths and angles, anisotropic displacement parameters, positional parameters, and least-squares planes for the crystal structures of **1–3** and an ORTEP drawing of the disorder model of **1** (68 pages); tables of observed and calculated structure factors (85 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[18] Unpublished results by W. A. Wojtczak, G. Chen, and F. A. Cotton.