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Zirconium Clusters from the Reaction of $ZrCl_4$ with $HSnBu_3$ Followed by Addition of Phosphines: $Zr_6Cl_{14}H_4(PR_3)_4$ Compounds

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The reduction of $ZrCl_4$ with $HSnBu_3$ followed by addition of phosphines yields pentanuclear cluster compounds $Zr_5Cl_{12}(PR_3)_5H_4$ (**2**) and three types of hexanuclear cluster compounds, $Zr_6Cl_{14}(PR_3)_4H_4$ (**3**), as well as $[Zr_6Cl_{18}H_5]^{3-}$ (**4**) and a small amount of $[Zr_6Cl_{18}H_4]^{4-}$ (**5**). Separation of these compounds has been achieved by using different solvents in which they have different solubilities and stabilities. The presence of hydrogen atoms and their numbers have been established by ^1H NMR spectroscopy. The compounds $Zr_6Cl_{14}(PR_3)_4H_4$ (**3a**, R = Me; **3b**, R = Et; **3c**, R = *n*-Pr) and $[HP(t\text{-}Bu)_2Ph]_3[Zr_6Cl_{18}H_5]$ (**4d**) have been characterized by X-ray crystallography. In compounds **3a** and **3b**, four hydrogen atoms distributed on the eight triangular faces of the Zr_6 octahedron were located. Compound **3a**·$2CH_2Cl_2$ crystallized in the monoclinic space group $P2_1/n$ with cell dimensions (−75 °C) of $a = 11.149(2)$ Å, $b = 11.049(4)$ Å, $c = 20.666(7)$ Å, $\beta = 103.42(2)°$, $V = 2476(1)$ Å^3, and $Z = 2$. Compound **3b**·$2CH_2Cl_2$ crystallized in orthorhombic space group *Pbca* with cell dimensions (−60 °C) of $a = 12.127(3)$ Å, $b = 21.793(5)$ Å, $c = 23.022(4)$ Å, $V = 6084(2)$ Å^3, and $Z = 4$. Compound **3c**·$2.31C_6H_6$ crystallized in triclinic space group $P\bar{1}$ with cell dimensions (−60 °C) of $a = 12.585(1)$ Å, $b = 13.679(2)$ Å, $c = 23.319(4)$ Å, $\alpha = 97.08(2)°$, $\beta = 94.77(2)°$, $\gamma = 93.30(2)°$, $V = 3960.6(9)$ Å^3, and $Z = 2$. Compound **4d**·$2CH_2Cl_2$·$2C_6H_6$ crystallized in monoclinic space group $C2/c$ with cell dimensions (−60 °C) of $a = 29.432(4)$ Å, $b = 13.503(1)$ Å, $c = 23.892(3)$ Å, $\beta = 110.96(1)°$, $V = 8867(2)$ Å^3, and $Z = 4$. In compounds **3a**−**c**, six zirconium atoms are arranged in a slightly elongated octahedron with four phosphine ligands at the equatorial positions. The distance of $Zr_{eq}-Zr_{ax}$ (3.359(8) Å) is slightly longer that of $Zr_{eq}-Zr_{eq}$ (3.308(6) Å), but both of them are shorter than that found in compound **4d** (3.416(2) Å).

Introduction

The synthesis of octahedral $Zr_6X_{12}Z$ type compounds has been achieved principally through high-temperature solid state reactions.[1] In these compounds, an atom of either a non-metal (Be, B, C, N)[2] or a metal (Fe, Co, Ni)[3] occupies the center of the cluster. By reducing ZrX_4 (X = Cl, Br) with $HSnBu_3$, we have developed a new method to prepare zirconium cluster compounds under mild reaction conditions (room temperature in organic solvents).[4−6] Reaction of $ZrCl_4$ with $HSnBu_3$ followed by addition of phosphonium or ammonium chlorides yielded products with the cluster anion $[Zr_6Cl_{18}H_5]^{3-}$, in which all the cluster hydrogen atoms are distributed over all eight triangular faces of the octahedron.[4] It was also found that the reduction of $ZrCl_4$ with 2.0 equiv of $HSnBu_3$ for 36 h followed by addition of 1.0 equiv of phosphines resulted in the formation of hexazirconium cluster compounds $Zr_6Cl_{14}(PR_3)_4H_4$ (**3**) in CH_2Cl_2 or MeCN.[6] By slight changes in the reaction conditions ($ZrCl_4$ reduced with 1.6 equiv of $HSnBu_3$ for 24 h), pentanuclear zirconium cluster compounds $Zr_5Cl_{12}(PR_3)_5H_4$ (**2**) were obtained.[5] In $Zr_5Cl_{12}(PMe_3)_5H_4$ (**2a**), four hydrogen atoms were located, with two of them on the triangular faces of the pyramidal cluster and the other two on the basal edges.[5] The compounds $[Zr_6Cl_{14}(PR_3)_4H_4]$ are extremely air and moisture sensitive. Paramagnetic species derived from the decomposition excluded the possibility of observing the cluster hydrogen at the time a preliminary report of their structures was published.[6] ^1H NMR study of scrupulously pure, crystalline samples in dry solvent revealed that there are four hydrogen atoms in the compounds $[Zr_6Cl_{14}(PR_3)_4H_4]$.

It is not possible to understand why the slightly different reaction conditions lead to totally different types of zirconium cluster compounds until we understand that their solubility and stability in different solvents vary greatly. Now we wish to report the results of separation and characterization of the products from the reduction of $ZrCl_4$ with $HSnBu_3$ followed by addition of phosphines. These products include $Zr_5Cl_{12}(PR_3)_5H_4$ (**2**), $Zr_6Cl_{14}(PR_3)_4H_4$ (**3**), $[Zr_6Cl_{18}H_5]^{3-}$ (**4**), and $[Zr_6Cl_{18}H_4]^{4-}$ (**5**). They are characterized by single-crystal X-ray diffraction analysis and ^1H NMR spectroscopy. A preliminary report of a portion of this work has been published.[6]

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. $ZrCl_4$, $HSnBu_3$, $DSnBu_3$, PMe_3, PEt_3, and PPr_3 were purchased from Strem Chemicals and used as received. $P(t\text{-}Bu)_2Ph$ was prepared by the literature method.[7] ^1H NMR spectra were collected on a Varian XL-200E or a Gemini 200 spectrometer.

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1996.

(1) For recent reviews see: (a) Corbett, J. D.; Garcia, E.; Kwon, Y.-U.; Guloy, A. *High Temp. Sci.* **1990**, *27*, 337. (b) Rogel, F.; Zhang, J.; Payne, M. W.; Corbett, J. D. *Adv. Chem. Ser.* **1990**, *226*, 369. (c) Corbett, J. D.; Ziebarth, R. P. *Acc. Chem. Res.* **1989**, *22*, 256.

(2) (a) Ziebarth, R. P.; Corbett, J. D. *J. Solid State Chem.* **1989**, *80*, 56. (b) Smith, J. D.; Corbett, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5704. (c) Zhang, J.; Corbett, J. D. *Z. Anorg. Allg. Chem.* **1991**, *598*, 363.

(3) (a) Hughbanks, T.; Rosenthal, G.; Corbett, J. D. *J. Am. Chem. Soc.* **1986**, *108*, 8289. (b) Hughbanks, T.; Rosenthal, G.; Corbett, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 1511.

(4) Chen, L.; Cotton, F. A.; Wojtczak, W. A. *Angew. Chem.* **1995**, *34*, 1877.

(5) Cotton, F. A.; Lu, J.; Shang, M.; Wojtczak, W. A. *J. Am. Chem. Soc.* **1994**, *116*, 4364.

(6) Cotton, F. A.; Feng, X.; Shang, M.; Wojtczak, W. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1050.

(7) Mann, B. E.; Shaw, B. L.; Slade, R. M. *J. Chem. Soc. A* **1971**, 2976.

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Reduction of $ZrCl_4$ with $HSnBu_3$. $ZrCl_4$ (466 mg, 2.0 mmol) was reduced with $HSnBu_3$ (1.15 mL, 4.0 mmol) in 20 mL of benzene with vigorous stirring for 30 h. The orange supernatant liquid was then decanted, and the precipitate was washed with two 10 mL portions of fresh benzene to give a brown solid **1** (*ca.* 500 mg after pumping under vacuum at room temperature for 2 h). The ^{1}H NMR spectrum of **1** in CD_3CN showed signals of butyl groups. It is believed brown solid **1** contains some unreacted $ZrCl_4$.

Reaction of 1 with PMe_3. Benzene (15 mL) was added to the brown solid **1**. To this reaction mixture was added 1.0 equiv of PMe_3 (0.20 mL, 2.0 mmol) dropwise by syringe with stirring, producing a brown solution, a dark red-brown solid on the wall of the flask, and a purple precipitate on the bottom. The brown solution was transferred to a Schlenk tube and layered with 30 mL of hexane. Dark brown crystals of $Zr_5Cl_{12}(PMe_3)_5H_4{\cdot}C_6H_6$ (**2a**$\cdot C_6H_6$)[5] appeared in 2 weeks. The isolated crystalline yield of **2**$\cdot C_6H_6$ was 71 mg (13%). Addition of 15 mL of CH_2Cl_2 to the remaining solids produced a red-brown solution. The purple precipitate was left undissolved on the bottom of the flask. The red-brown solution was transferred to a Schlenk tube and layered with 30 mL of hexane. Dark red-brown crystals of $Zr_6Cl_{14}(PMe_3)_4H_4{\cdot}2CH_2Cl_2$ (**3a**$\cdot 2CH_2Cl_2$) were formed within 1 week. The isolated crystalline yield was 92 mg (18%). ^{1}H NMR (in CD_3CN, ppm): 1.80 (d, $^3J_{P-H} = 15$ Hz, PCH_3, 36H), -5.18 (s, br, Zr*H*, 4H). The remaining purple solid was also insoluble in MeCN and THF and decomposed in pyridine and MeOH. It has not been investigated further because of its insolubility.

Reaction of 1 with PEt_3. This reaction was carried out as described above by using PEt_3 (0.29 mL, 2.0 mmol) instead of PMe_3. The isolated crystalline yields for $Zr_5Cl_{12}(PEt_3)_5H_4{\cdot}C_6H_6$ (**2b**$\cdot C_6H_6$)[5] and $Zr_6Cl_{14}(PEt_3)_4H_4{\cdot}2CH_2Cl_2$ (**3b**$\cdot 2CH_2Cl_2$) were 80 mg (14%) and 91 mg (16%), respectively. ^{1}H NMR for compound **3b** (in CD_3CN, ppm): 2.11 (m, PCH_2CH_3, 24H), 1.17 (m, PCH_2CH_3, 36H), -4.94 (s, br, Zr*H*, 4H). The remaining purple solid was pumped dry and dissolved in 15 mL of MeCN. The resulting purple solution was transferred to a Schlenk tube and layered with 2 mL of hexane and then 30 mL of Et_2O. About 26 mg of tiny dark purple crystals, too small for single-crystal X-ray diffraction study, were obtained in 10 days. ^{1}H NMR (in CD_3CN) showed they are a mixture of $[Zr_6Cl_{18}H_5]^{3-}$ (**4**) (-3.05 ppm)[4] and $[Zr_6Cl_{18}H_4]^{4-}$ (**5**) (-5.17 ppm)[4] (mole ratio of **4** to **5** was 10:1) with cations $MePEt_3^+$ (1.70 ppm, d, $^3J_{P-H} = 14$ Hz, PCH_3) and $HPEt_3^+$ (5.70 ppm, doublet of septets, $^2J_{P-H} = 478$ Hz, $^3J_{H-H} = 5$ Hz, $HP(CH_2CH_3)_3$) (mole ratio of $MePEt_3^+$ to $HPEt_3^+$ was 1:4).

Reaction of PEt_3 with $HSnBu_3$ in CH_2Cl_2. A solution of PEt_3 (0.29 mL, 2.0 mmol) and $HSnBu_3$ (0.57 mL, 2.0 mmol) in 20 mL of CH_2Cl_2 was stirred at 20 °C for 24 h. The solvent was removed under vacuo. The solid mixture was analyzed by ^{1}H NMR showing the presence of $MePEt_3^+$.

Reaction of 1 with PPr_3. Benzene (15 mL) was added to the brown solid **1** followed by addition of 1.0 equiv of PPr_3 (0.40 mL, 2.0 mmol) dropwise by syringe with stirring. This produced a red-brown solution and a purple solid on the wall of the flask. The red-brown solution was transferred to a Schlenk tube and layered with 30 mL of hexane. Dark red-brown crystals of $Zr_6Cl_{14}(PPr_3)_4H_4{\cdot}2.31C_6H_6$ (**3c**$\cdot 2.31C_6H_6$) began to appear in 2 weeks. The crystalline yield of **3c**$\cdot 2.31C_6H_6$ was 102 mg (15%). ^{1}H NMR (in CD_3CN, ppm) for **3c**: 2.25 (m, $PCH_2CH_2CH_3$, 24H), 1.73 (m, $PCH_2CH_2CH_3$, 24H), 0.97 (m, $PCH_2CH_2CH_3$, 36H), -5.09 (s, br, Zr*H*, 4H). An attempt to isolate $Zr_5Cl_{12}(PPr_3)_5H_4$ was unsuccessful although the ^{1}H NMR spectrum of the reaction mixture in CD_2Cl_2 showed a signal at -1.60 ppm, which might be attributed to $Zr_5Cl_{12}(PPr_3)_5H_4$. To the remaining purple solid was added 15 mL of CH_2Cl_2. The resulting purple solution was transferred to a Schlenk tube and layered with 30 mL of hexane. Purple crystals of $[HPPr_3]_3[Zr_6Cl_{18}H_5]$ (**4c**) were formed in 3 days. The crystalline yield was 89 mg (16%). ^{1}H NMR (in CD_3CN, ppm) for **4c**: 5.97 (doublet of septets, $^2J_{P-H} = 473$ Hz, $^3J_{H-H} = 5$ Hz, $HP(CH_2CH_2CH_3)_3$, 3H), 2.15 (m, $HP(CH_2CH_2CH_3)_3$, 18H), 1.63 (m, $HPCH_2CH_2CH_3)_3$, 18H), 1.28 (m, $HP(CH_2CH_2CH_3)_3$, 27H), -3.05 (s, br, Zr*H*, 5H).

When $ZrCl_4$ was reduced with $DSnBu_3$, the products from the reaction of brown solid **1** with PPr_3 were Zr_6Cl_{14} $(PPr_3)_4D_4$ (**3c***) and $[DPPr_3]_3[Zr_6Cl_{18}D_5]$ (**4c***). The ^{1}H NMR signals due to cluster hydrogen atoms and protons bonded to phosphorus were not observed.

Reaction of 1 with $P(t\text{-}Bu)_2Ph$. To the brown solid **1** were added 15 mL of CH_2Cl_2 and then 1.0 equiv of $P(t\text{-}Bu)_2Ph$. The brown solid was solubilized gradually, producing a purple solution. This purple solution was transferred to a Schlenk tube and layered with 30 mL of hexane. A 154 mg (21%) yield of purple crystals of $[HP(t\text{-}Bu)_2Ph]_3[Zr_6Cl_{18}H_5]{\cdot}2CH_2Cl_2{\cdot}2C_6H_6$ (**4d**$\cdot 2CH_2Cl_2\cdot 2C_6H_6$) was obtained in 1 week. ^{1}H NMR (in CD_3CN, ppm): 7.76 (m, $(C_6H_5)P$, 15H), 4.34 (d, $^2J_{P-H} = 427$ Hz, *H*P, 3H), 1.42 (s, $P(C(CH_3)_3)$, 54H), -3.03 (s, br, Zr*H*, 5H).

X-ray Crystallography

Each crystal that was used in diffraction intensity measurements was mounted on the tip of a quartz fiber and placed in a cold stream of nitrogen. Diffraction measurements were made on an Enraf-Nonius CAD-4 automated diffractometer with graphite-monochromated Mo Kα radiation for compounds **3a**$\cdot 2CH_2Cl_2$ and **3b**$\cdot 2CH_2Cl_2$ and on an Enraf-Nonius FR590 diffractometer equipped with an area detector and Mo Kα radiation for compounds **3c**$\cdot 2.31C_6H_6$ and **4d**$\cdot 2CH_2Cl_2\cdot 2C_6H_6$. For the crystals on the CAD-4 diffractometer, unit cells were determined by using search, center, index, and least-squares routines. The Laue classes and lattice dimensions were verified by axial oscillation photography. The intensity data were corrected for Lorentz and polarization effects and for anisotropic decay. Empirical absorption corrections based on ψ scans were also applied. For the crystals on the FR590 diffractometer, preliminary data collection was carried out first to afford all parameters and an orientation matrix. Fifty reflections were used in indexing and 250 reflections in cell refinement. Axial images were obtained to determine the Laue group and cell dimensions. No decay corrections were applied. Diffast was used for an absorption correction for compound **3c**$\cdot 2.31C_6H_6$. Diffast is a modification of diffabs for the area detector.[8]

Each structure was solved by a combination of direct methods using the SHELXS-86 program[9a] and difference Fourier analyses using the SHELXL-93 program.[9b] Crystallographic data and results of analyses are listed in Table 1.

Compound **3a**$\cdot 2CH_2Cl_2$ crystallized in the monoclinic crystal system. The space group $P2_1/n$ was identified uniquely from the systematic absences in the data. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms, including the cluster hydrogen atoms and those on the CH_2Cl_2 of crystallization, were located following complete anisotropic refinement of all other atoms and refined isotropically. Although the cluster hydrogen atoms were located without difficulty, the results of refinement on their occupancies and the positions for H(2) and H(4) were not satisfactory because of the thermal movement at the measurement temperature and the presence of heavy atoms nearby. Fixed occupancies for all cluster hydrogen atoms (H(1), 40%; H(2), 48%; H(3), 100%; H(4), 12%) and fixed positions for H(2) and H(4) were employed in the refinement. The total number of 4 of the cluster hydrogen atoms was inferred from the ^{1}H NMR study.

Compound **3b**$\cdot 2CH_2Cl_2$ crystallized in the orthorhombic crystal system. The systematic absences in the data set uniquely defined the space group as *Pbca* (No. 61). The carbon atoms of the disordered phosphine ligand were refined isotropically. The other non-hydrogen atoms were refined with anisotropic thermal parameters. Four cluster hydrogen atoms were located and refined with fixed occupancies (H(1), 64%; H(2), 76%; H(3), 9%; H(4), 51%) and with fixed positions for H(1), H(3), and H(4) for the same reason mentioned above. The positions of hydrocarbon hydrogen atoms were calculated by assuming idealized geometries, C−H = 0.99 Å for methyl groups and C−H = 0.98 Å for methylene groups. They were refined with fixed thermal parameters of 1.2 and 1.5 times the B^c_{eqv} of the corresponding carbon atom, respectively.

Compound **3c**$\cdot 2.31C_6H_6$ crystallized in a triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by successful solution

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[8] Walker, N. P.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.

[9] (a) Sheldrick, G. M. *SHELXS-86: Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1986. (b) Sheldrick, G. M. *SHELXL-93: Fortran-77 program for the refinement of crystal structures from diffraction data*; University of Göttingen: Göttingen, Germany, 1993.

Table 1. Crystal Data for **3a**$\cdot 2CH_2Cl_2$, **3b**$\cdot 2CH_2Cl_2$, **3c**$\cdot 2.31C_6H_6$, and **4d**$\cdot 2CH_2Cl_2 \cdot 2C_6H_6$

	3a$\cdot 2CH_2Cl_2$	**3b**$\cdot 2CH_2Cl_2$	**3c**$\cdot 2.31C_6H_6$	**4d**$\cdot 2CH_2Cl_2 \cdot 2C_6H_6$
formula	$C_{14}H_{44}Cl_{18}P_4Zr_6$	$C_{26}H_{68}Cl_{18}P_4Zr_6$	$C_{49.86}H_{97.86}Cl_{14}P_4Zr_6$	$C_{56}H_{93}Cl_{22}P_3Zr_6$
fw	1521.79	1690.1	1864.97	2186.56
crystal system	monoclinic	orthorhombic	triclinic	monoclinic
space group	$P2_1/n$	*Pbca*	$P\bar{1}$	$C2/c$
a, Å	11.149(2)	12.127(3)	12.585(1)	29.432(4)
b, Å	11.049(4)	21.793(5)	13.679(2)	13.503(1)
c, Å	20.666(7)	23.022(4)	23.319(4)	23.892(3)
α, deg	90	90	97.08(2)	90
β, deg	103.42(2)	90	94.77(2)	110.96(1)
γ, deg	90	90	93.30(2)	90
V, $Å^3$	2476(1)	6084(2)	3960.6(9)	8867(2)
Z	2	4	2	4
d_{calc}, g/cm^3	2.041	1.845	1.576	1.679
μ, cm^{-1}	23.3	19.07	13.43	14.83
data collection instrument	CAD-4	CAD-4	FR590	FR590
radiation (monochromated)	Mo Kα (λ = 0.709 30 Å)	Mo Kα (λ = 0.709 30 Å)	Mo Kα (λ = 0.709 30 Å)	Mo Kα (λ = 0.709 30 Å)
temp, °C	−75	−60	−60	−60
$2\theta_{max}$, deg	46	46	40	40
no. of observns ($I > 2\sigma(I)$)	2871	3553	5366	2637
no. of variables	280	249	673	438
residuals: R1,[a] wR2[b]	0.040, 0.090	0.063, 0.136	0.073, 0.150	0.076, 0.143
quality-of-fit indicator[c]	0.945	1.102	1.051	1.153
max shift in final cycle	0.02	0.003	0.011	0.005
largest peak, e/$Å^3$	1.0(2)	1.0(2)	1.0(1)	1.7(1)
absorption correction	empirical	empirical	diffast	none

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ (based on reflections with $F_o^2 > 2\sigma(F_o^2)$). [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$; $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$ (also with $F_o^2 > 2\sigma(F_o^2)$). [c] Quality-of-fit (on F^2) = $[\sum[w(F_o^2 - F_c^2)^2]/(N_{observns} - N_{params})]^{1/2}$.

and refinement of the structure. Carbon atoms C(441), C(442), C(451), C(452), C(461), and C(462) on the disordered phosphine ligand were refined isotropically. The other non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of hydrogen atoms were calculated by assuming idealized geometries, C−H = 0.98 Å for methyl groups, C−H = 0.97 Å for methylene groups, and C−H = 0.93 Å for benzene. They were refined with fixed thermal parameters of $1.2B^c_{eqv}$ for methylene groups and benzene and $1.5B^c_{eqv}$ for methyl groups.

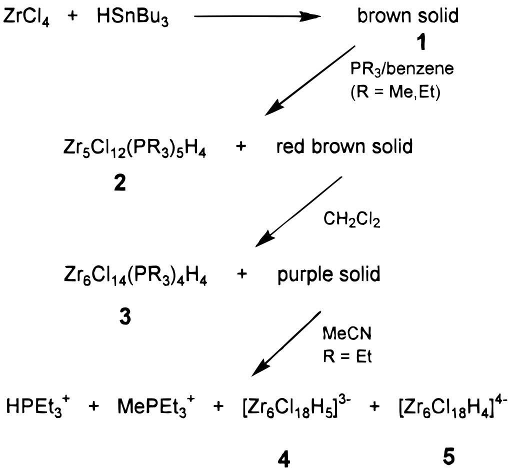
Compound **4d**$\cdot 2CH_2Cl_2 \cdot 2C_6H_6$ crystallized in the monoclinic crystal system. The systematic absences in the data were consistent with either space group *C*2/*c* or *Cc*. The centrosymmetric space group *C*2/*c* was assumed and confirmed by the successful solution and refinement of the structure. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were dealt with as described for the previous cases. One of the chlorine atoms of CH_2Cl_2 was found to be disordered at two positions.

Results and Discussion

Reduction of $ZrCl_4$ with $HSnBu_3$ produced a brown solid, **1**. Reaction of **1** with phosphines yielded a series of pentanuclear and hexanuclear zirconium cluster compounds. The products include neutral compounds $Zr_5Cl_{12}(PR_3)_5H_4$ (**2**) and $Zr_6Cl_{14}(PR_3)_4H_4$ (**3**) and compounds containing $[Zr_6Cl_{18}H_5]^{3-}$ (**4**) and $[Zr_6Cl_{18}H_4]^{4-}$ (**5**) ions. The structures of the pentanuclear compounds **2a** and **2b** were described in a previous report.[5] We have found that the pentanuclear zirconium compounds $Zr_5Cl_{12}(PR_3)_5H_4$ (**2**) decompose slowly in CH_2Cl_2 solution and that the hexanuclear zirconium compounds $Zr_6Cl_{14}(PR_3)_4H_4$ (**3**) are gradually converted to $[Zr_6Cl_{18}H_4]^{4-}$ (**5**) in CH_3CN solution.[10] By using different solvents with different polarities and reactivities toward the products, we have been successful in isolating all the cluster products observed in the ^1H NMR spectra for the reaction mixture. The general sequence is outlined in Scheme 1.

Two compounds were isolated from the reaction of brown solid **1** of reduced $ZrCl_4$ with PMe_3. The solubility of $Zr_6Cl_{14}(PMe_3)_4H_4$ (**3a**) in benzene was found to be very low. Only $Zr_5Cl_{12}(PMe_3)_5H_4$ (**2a**) is soluble in benzene. This makes it possible to separate compound **2a** from the rest of the products. For the remaining product mixture, only compounds **2a** and **3a** are soluble in CH_2Cl_2. The small amount of compound **2a** left due to the incomplete separation was decomposed in CH_2Cl_2 during crystallization. The only crystalline product from the CH_2Cl_2 solution was compound **3a**. Attempts to isolate the ionic products from the purple solid were unsuccessful because of its extremely low solubility.

Scheme 1



Compound **3a** was characterized by ^1H NMR and single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of **3a** without the hydrogen atoms is shown in Figure 1. Selected bond distances and angles are listed in Table 2. There are two distinct sets of Zr−Zr bond lengths corresponding to a small but real tetragonal distortion. The average of the four distances between two phosphine-coordinated zirconium atoms, Zr(P)−Zr(P), is about 0.05 Å shorter than those between a phosphine-coordinated zirconium atom and a terminal chlorine-coordinated zirconium atom, Zr(P)−Zr(Cl), namely, 3.302(1) Å vs 3.351(1) Å. This phenomenon has been observed before[2a] in solid-state clusters of the composition $[Zr_6X_{14}Z]^{n+}$ and may be attributed to the chemical

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(10) Chen, L.; Cotton, F. A.; Wojtczak, W. A. Submitted to *Inorg. Chim. Acta.*

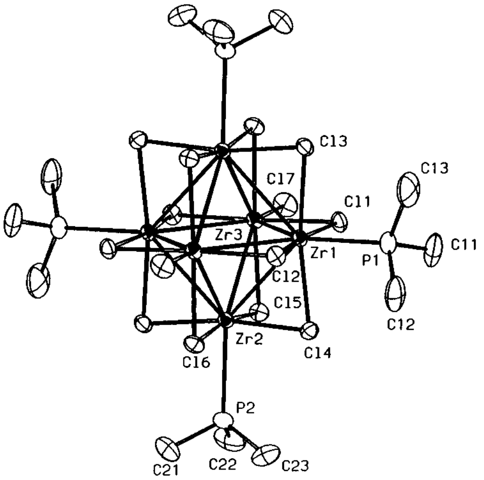

Figure 1. ORTEP drawing of the $Zr_6Cl_{14}(PMe_3)_4H_4$ (**3a**) molecule without cluster hydrogen atoms. Atoms are represented by their ellipsoids at the 50% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Zr_6Cl_{14}(PMe_3)_4H_4 \cdot 2CH_2Cl_2$ (**3a**·2CH$_2$Cl$_2$)[a]

Zr(1)−Zr(2)′	3.297(1)	Zr(3)−Cl(6)′	2.567(2)
Zr(1)−Zr(2)	3.307(1)	Zr(3)−Cl(2)′	2.577(2)
Zr(1)−Zr(3)	3.345(1)	Zr(3)−Cl(5)	2.582(2)
Zr(2)−Zr(1)′	3.297(1)	Zr(1)−P(1)	2.752(2)
Zr(2)−Zr(3)′	3.354(1)	Zr(2)−P(2)	2.761(2)
Zr(3)−Zr(1)′	3.352(1)	Zr(1)−H(4)	1.5830(8)
Zr(3)−Zr(2)′	3.354(1)	Zr(1)−H(1)	1.8(2)
Zr(1)−Cl(1)	2.546(2)	Zr(1)−H(3)	1.99(2)
Zr(1)−Cl(2)	2.548(2)	Zr(1)−H(2)	2.2532(9)
Zr(1)−Cl(3)	2.554(2)	Zr(2)−H(3)′	1.82(8)
Zr(1)−Cl(4)	2.569(2)	Zr(2)−H(1)	1.98(2)
Zr(2)−Cl(6)	2.548(2)	Zr(2)−H(2)	2.0565(9)
Zr(2)−Cl(5)	2.557(2)	Zr(2)−H(4)′	2.3697(9)
Zr(2)−Cl(3)′	2.556(2)	Zr(3)−H(2)′	1.5431(8)
Zr(2)−Cl(4)	2.569(2)	Zr(3)−H(3)	1.96(8)
Zr(3)−Cl(7)	2.495(2)	Zr(3)−H(1)	2.0(1)
Zr(3)−Cl(1)	2.566(2)	Zr(3)−H(4)′	2.2782(7)
		Zr−H(av)	2.0(2)
Zr(2)′−Zr(1)−Zr(2)	90.40(3)	Zr(2)−Cl(6)−Zr(3)′	81.93(6)
Zr(1)′−Zr(2)−Zr(1)	89.60(3)	Zr(1)−H(1)−Zr(2)	120(10)
Zr(1)−Zr(3)−Zr(1)′	88.02(3)	Zr(1)−H(1)−Zr(3)	122(4)
Zr(2)′−Zr(1)−Zr(3)	60.65(3)	Zr(2)−H(1)−Zr(3)	115(9)
Zr(2)−Zr(1)−Zr(3)	60.81(3)	Zr(3)′−H(2)−Zr(2)	136.93(4)
Zr(1)′−Zr(2)−Zr(3)′	60.38(3)	Zr(3)′−H(2)−Zr(1)	122.93(3)
Zr(1)−Zr(2)−Zr(3)′	60.44(2)	Zr(2)−H(2)−Zr(1)	100.11(3)
Zr(1)−Zr(3)−Zr(2)′	58.97(2)	Zr(2)′−H(3)−Zr(3)	125(1)
Zr(1)′−Zr(3)−Zr(2)′	59.08(3)	Zr(2)′−H(3)−Zr(1)	120(4)
Zr(1)−Cl(1)−Zr(3)	81.74(6)	Zr(3)−H(3)−Zr(1)	115(4)
Zr(1)−Cl(2)−Zr(3)′	81.71(5)	Zr(1)−H(4)−Zr(3)′	119.42(3)
Zr(1)−Cl(3)−Zr(2)′	80.36(5)	Zr(1)−H(4)−Zr(2)′	111.50(3)
Zr(1)−Cl(4)−Zr(2)	80.12(6)	Zr(3)′−H(4)−Zr(2)′	92.80(3)
Zr(2)−Cl(5)−Zr(3)	81.86(6)	Zr−H−Zr(av)	117(9)

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

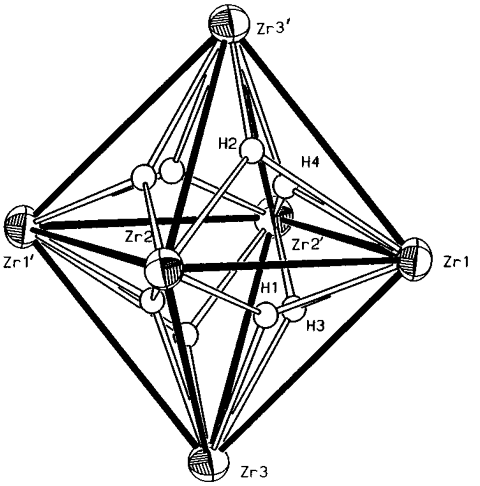

Figure 2. ORTEP drawing of the Zr_6H_4 unit in the $Zr_6Cl_{14}(PMe_3)_4H_4$ (**3a**) molecule. Hydrogen atoms have been given arbitrary thermal parameters for clarity. Zr atoms are represented by their ellipsoids at the 50% probability level.

inequality of Zr(P) and Zr(Cl), resulting from the disparate electron-donor ability of the terminal ligands. There are also three sets of bond lengths between Zr and bridging Cl atoms: one between a phosphine-coordinated Zr atom and a Cl atom bridging over two phosphine-coordinated Zr atoms, Zr(P)−Cl(ZrP,ZrP) = 2.562(2) Å, one between a phosphine-coordinated Zr atom and a Cl atom bridging over one phosphine-coordinated Zr atom and one terminal-Cl-coordinated Zr atom, Zr(P)−Cl(ZrP,ZrCl) = 2.550(2) Å, and one between a terminal-Cl-coordinated Zr atom and a Cl atom bridging over one phosphine-coordinated Zr atom and one terminal-Cl-coordinated Zr atom, Zr(Cl)−Cl(ZrP,ZrCl) = 2.573(2) Å. As expected, the Zr to terminal-Cl distance is shorter, 2.495(2) Å. The average Zr−P bond length is 2.756(2) Å.

Four hydrogen atoms have been found on or near the centers of eight triangular faces of the octahedron with partial occupancies as in $[Zr_6Cl_{18}H_5]^{3-}$ with five cluster hydrogen atoms. This is consistent with the ^{1}H NMR data. The signal due to these hydrogen atoms appeared at −5.18 ppm. The peak is broad ($\Delta\nu_{1/2}$ = 4.4 Hz), and no obvious P−H coupling was observed. The average distance between Zr and H atoms is 2.0(2) Å, which is effectively equal to the values of 1.96(8) Å in the pentanuclear compound **2a**[5] and 1.97(2) Å in the hexanuclear compound $[Ph_4P]_3[Zr_6Cl_{18}H_5]$.[4] An ORTEP diagram of the Zr_6H_4 unit is shown in Figure 2. This is the first time that we have been able to locate the hydrogen atoms for one of the $Zr_6Cl_{14}(PR_3)_4H_4$ type compounds. However, the results are not fully satisfactory. It should be noted that although electron density was observed at the triangular centers unambiguously, the occupancies are not as reliable because of the thermal movement of hydrogen atoms and the presence of heavy atoms. We are searching for a better data set on such a compound. Work toward single-crystal neutron diffraction is also in progress.

There are only a few examples of M_6 octahedral compounds containing two or more hydrogen atoms. In the clusters $[Ph_4P]_3[Zr_6Cl_{18}H_5]$,[4] $Th_6Br_{15}H_7$,[11] $H_6Cu_6(PR_3)_6$,[12] and $H_2Ru_6(CO)_{18}$,[13] the cluster hydrogen atoms are known or believed to reside on or above the centers of the triangular faces of the M_6 octahedron. As we previously reported, five cluster hydrogen atoms in the $[Zr_6Cl_{18}H_5]^{3-}$ ion have been found and refined, at partial occupancy, at or very near the centers of all triangular faces of the Zr_6 octahedron from single-crystal X-ray diffraction data.[4] The location of the hydrogen atoms in the $Th_6Br_{15}H_7$ cluster was determined from a neutron powder diffraction experiment on the deuterated analog, $Th_6Br_{15}D_7$,[11] Th−D = 2.238(2) Å. Seven deuterons were found statistically disordered

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(11) (a) Böttcher, F.; Simon, A.; Kremer, R. K.; Buchkremer-Hermanns, H.; Cockcroft, J. K. *Z. Anorg. Allg. Chem.* **1991**, *598*, 25. (b) Simon, A.; Böttcher, F.; Cockcroft, J. K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 101.

(12) (a) Bezman, S. A.; Churchill, M. R.; Osborn, J. A.; Wormald, J. *J. Am. Chem. Soc.* **1971**, *93*, 2063. (b) Churchill, M. R.; Bezman, S. A.; Osborn, J. A.; Wormald, J. *Inorg. Chem.* **1972**, *11*, 1818. (c) Stevens, R. C.; Maclean, M. R.; Bau, R. *J. Am. Chem Soc.* **1989**, *111*, 3472. (d) Lemmen, T. H.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem.* **1985**, *107*, 7774.

(13) Churchill, M. R.; Wormald, J. *J. Am. Chem. Soc.* **1971**, *93*, 5670.

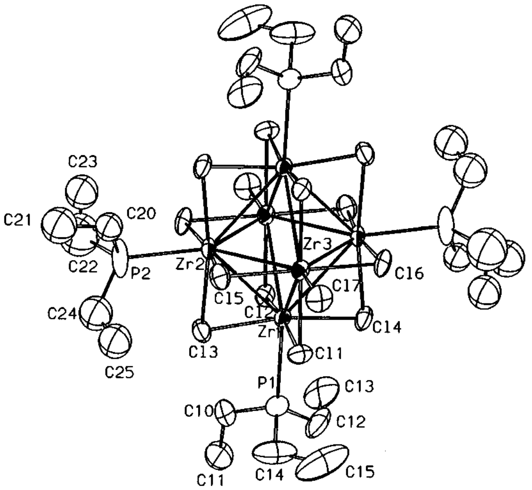


Figure 3. ORTEP drawing of the $Zr_6Cl_{14}(PEt_3)_4H_4$ (**3b**) molecule without cluster hydrogen atoms. Atoms are represented by their ellipsoids at the 50% probability level.

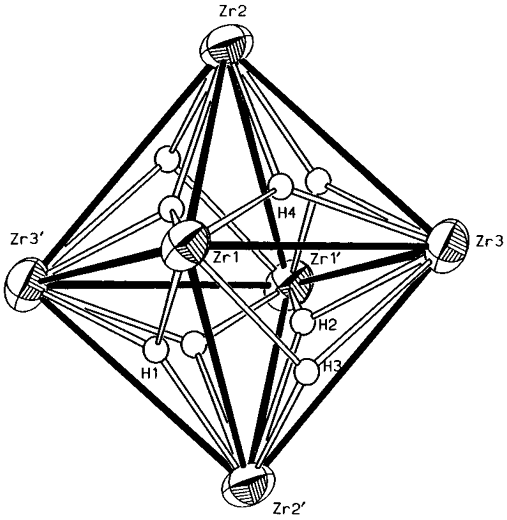


Figure 4. ORTEP drawing of the Zr_6H_4 unit in the $Zr_6Cl_{14}(PEt_3)_4H_4$ (**3b**) molecule. Hydrogen atoms have been given arbitrary thermal parameters for clarity. Zr atoms are represented by their ellipsoids at the 50% probability level.

over the eight trigonal faces of the Th_6 octahedron. The presence of the hydrogen atoms on the $H_6Cu_6(PR_3)_6$ clusters was first inferred from NMR results and from the six long and six short Cu−Cu distances of the Cu_6 octahedron.[12a−c] The location of the hydrogen atoms on the outside of six of the Cu_3 triangular faces of the Cu_6 octahedron was then established by single-crystal neutron diffraction (R = *p*-tolyl) (Cu−H = 1.76(3) Å)[12b,c] and low-temperature X-ray diffraction (R = NMe_2) (Cu−H = 1.71(8) Å)[12d] experiments. For $H_2Ru_6(CO)_{18}$, the presence of hydrogen atoms was inferred from mass spectrometry results, and their location was inferred from the X-ray structural results, which showed terminal carbonyl groups bent away from two enlarged Ru_3 faces.[12]

Reaction of the brown solid **1** with PEt_3 was carried out similarly to that for PMe_3. In addition to the two neutral products, the pentanuclear compound $Zr_5Cl_{12}(PEt_3)_5H_4$ (**2b**) and the hexanuclear compound $Zr_6Cl_{14}(PEt_3)_4H_4$ (**3b**), two ionic species, $[Zr_6Cl_{18}H_5]^{3-}$ (**4**), and $[Zr_6Cl_{18}H_4]^{4-}$ (**5**), were obtained by using MeCN as extraction solvent. ^1H NMR study showed that species **4** and **5** crystallized with ions $[HPEt_3]^+$ and/or $[MePEt_3]^+$. $Zr_6Cl_{14}(PR_3)_4H_4$ is not stable in MeCN solution. It was converted slowly into $[HPR_3]_4[Zr_6Cl_{18}H_4]$ in *ca.* 50% yield.[4] It is very possible that the $[Zr_6Cl_{18}H_4]^{4-}$ anion and the $[HPEt_3]^+$cation present in the mixture were formed in a similar way. Compounds containing the $[Zr_6Cl_{18}H_5]^{3-}$ (**4**) cluster may be prepared easily from the reaction of the brown solid **1** with ammonium or phosphonium chloride.[4] It is believed the $[Zr_6Cl_{18}H_5]^{3-}$ anion observed in the mixture was from the reaction of the brown solid **1** with the Cl^- ion in the solution. The $[MePEt_3]^+$ cation was also observed in the mixture by ^1H NMR, and it has been observed in the crystalline compound $[MePEt_3]_2[Ph_4P]_2[Zr_6Cl_{18}H_4]$.[10] We propose that it was formed from the reaction of PEt_3 with residual $HSnBu_3$ and CH_2Cl_2.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Zr_6Cl_{14}(PEt_3)_4H_4{\cdot}2CH_2Cl_2$ (**3b**$\cdot 2CH_2Cl_2$)[a]

Zr(1)−Zr(2)	3.304(1)	Zr(3)−Cl(5)	2.565(3)
Zr(1)−Zr(2)′	3.308(1)	Zr(3)−Cl(1)	2.566(3)
Zr(1)−Zr(3)	3.355(2)	Zr(1)−P(1)	2.779(3)
Zr(2)−Zr(3)	3.358(2)	Zr(2)−P(2)	2.792(3)
Zr(3)−Zr(2)′	3.359(2)	Zr(1)−H(3)	1.999(1)
Zr(1)−Cl(1)	2.548(3)	Zr(1)−H(1)	2.036(1)
Zr(1)−Cl(2)	2.550(3)	Zr(1)−H(4)	2.036(1)
Zr(1)−Cl(3)	2.554(3)	Zr(1)−H(2)′	2.0(1)
Zr(1)−Cl(4)	2.559(3)	Zr(2)−H(1)′	1.791(1)
Zr(2)−Cl(5)	2.540(3)	Zr(2)−H(4)	1.827(1)
Zr(2)−Cl(6)′	2.545(3)	Zr(2)−H(2)′	1.9(1)
Zr(2)−Cl(3)	2.551(3)	Zr(2)−H(3)′	1.946(1)
Zr(2)−Cl(4)′	2.569(3)	Zr(3)−H(4)	1.965(1)
Zr(3)−Cl(7)	2.500(3)	Zr(3)−H(2)	2.0(1)
Zr(3)−Cl(2)′	2.556(3)	Zr(3)−H(1)′	1.969(1)
Zr(3)−Cl(6)	2.562(3)	Zr(3)−H(3)	2.306(1)
		Zr−H(av)	2.0(1)

Zr(2)−Zr(1)−Zr(2)′	90.03(3)	Zr(2)′−Cl(6)−Zr(3)	82.25(8)
Zr(1)−Zr(2)−Zr(1)′	89.97(3)	Zr(2)′−H(1)−Zr(3)′	126.46(4)
Zr(2)−Zr(3)−Zr(2)′	88.24(3)	Zr(2)′−H(1)−Zr(1)	119.44(4)
Zr(2)−Zr(1)−Zr(3)	60.56(3)	Zr(3)′−H(1)−Zr(1)	114.07(4)
Zr(2)′−Zr(1)−Zr(3)	60.55(3)	Zr(2)′−H(2)−Zr(3)	121(5)
Zr(1)−Zr(2)−Zr(3)	60.47(3)	Zr(2)′−H(2)−Zr(1)′	114(5)
Zr(1)′−Zr(2)−Zr(3)	60.55(3)	Zr(3)−H(2)−Zr(1)′	113(5)
Zr(1)−Zr(3)−Zr(2)	58.97(3)	Zr(2)′−H(3)−Zr(1)	113.96(4)
Zr(1)−Zr(3)−Zr(2)′	59.02(3)	Zr(2)′−H(3)−Zr(3)	104.05(4)
Zr(1)−Cl(1)−Zr(3)	82.01(8)	Zr(1)−H(3)−Zr(3)	102.18(4)
Zr(2)−Cl(5)−Zr(3)	82.26(8)	Zr(2)−H(4)−Zr(3)	124.59(4)
Zr(1)−Cl(4)−Zr(2)′	80.32(8)	Zr(2)−H(4)−Zr(1)	117.46(4)
Zr(2)−Cl(3)−Zr(1)	80.66(8)	Zr(3)−H(4)−Zr(1)	113.95(4)
Zr(1)−Cl(2)−Zr(3)′	82.33(8)	Zr−H−Zr(av)	115(5)

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

Compound **3b** was also characterized by ^1H NMR and single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of **3b** without the hydrogen atoms is shown in Figure 3. Selected bond distances and angles are listed in Table 3. There are again two distinct sets of Zr−Zr bond lengths, Zr(P)−Zr(P) = 3.306(1) Å and Zr(P)−Zr(Cl) = 3.357(2) Å. Both are slightly longer than their counterparts in compound **3a**. Three sets of bond lengths between Zr and bridging Cl atoms exist too: Zr(P)−Cl(ZrP,ZrP) = 2.558(3) Å, Zr(P)−Cl(ZrP,ZrCl) = 2.546(3) Å, and Zr(Cl)−Cl(ZrP,ZrCl) = 2.562(3) Å. These are all slightly shorter than those found in compound **3a**. The distance between a Zr atom and a terminal Cl atom is essentially the same, Zr−Clt = 2.500(3) Å, but the average Zr to P distance is longer, 2.785(3) Å.

^1H NMR spectra indicated there are four hydrogen atoms in compound **3b** also. The hydrogen signal was observed at −4.94 ppm. Again this signal was broad ($\Delta\nu_{1/2}$ = 2.7 Hz) but showed no explicit sign of P−H coupling. The hydrogen atoms were again found at or near the centers of the eight triangular faces of the octahedron with partial occupancy. The distance between Zr and H atoms is 2.0(1) Å. An ORTEP diagram of the Zr_6H_4 unit is shown in Figure 4.

Although the reaction of brown solid **1** with PPr_3 was virtually the same as the reactions with PMe_3 and PEt_3 discussed above,

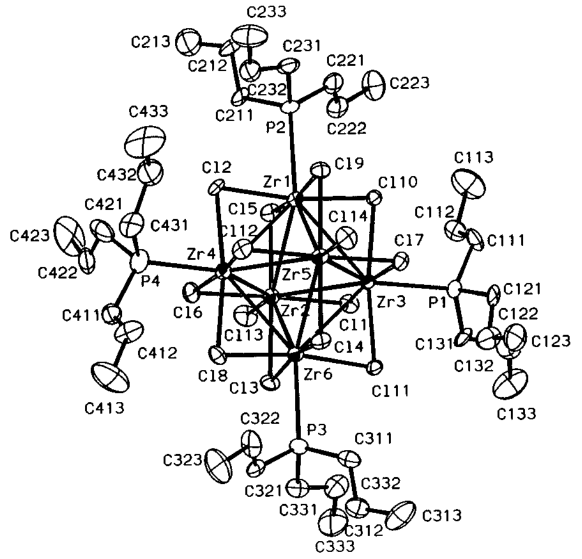
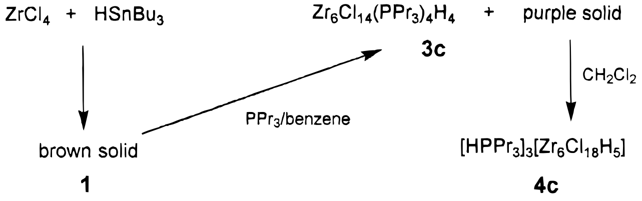


Figure 5. ORTEP drawing of the $Zr_6Cl_{14}(PPr_3)_4H_4$ (**3c**) molecule without cluster hydrogen atoms. Atoms are represented by their ellipsoids at the 50% probability level.

Scheme 2



the solubility of the product differs, as one might expect for PPr_3 with longer hydrocarbon chains. The reaction is summarized in Scheme 2. The reaction produced a red-brown solution and a purple solid. The red-brown solution contained $Zr_6Cl_{14}(PPr_3)_4H_4$ (**3c**) and probably $Zr_5Cl_{12}(PPr_3)_5H_4$ (**2c**) as shown by ^1H NMR spectra. The broad cluster hydrogen signal ($\Delta\nu_{1/2}$ = 3.4 Hz) of compound **3c** was found at −5.09 ppm. Unfortunately, we were unable to isolate compound **2c** in pure form although we did observe a hydrogen signal at −1.60 ppm in CD_2Cl_2 solution, which we attribute to compound **2c**. In CD_2Cl_2 solution, the hydrogen signals for compounds **2a** and **2b** were found at −2.04 and −1.22 ppm, respectively. Only compound **3c** crystallized from the solution. From the remaining purple solid, the compound $[HPPr_3]_3[Zr_6Cl_{18}H_5]$, **4c**, was isolated. It was characterized by ^1H NMR spectroscopy. The cluster hydrogen atoms appeared at −3.05 ppm, as expected for the anion $[Zr_6Cl_{18}H_5]^{3-}$,[4] and the number of hydrogen atoms was inferred to be 5 from integrating the cluster hydrogen signal against those for the cation $[HPPr_3]^+$. The hydrogen atom bonded to the phosphorus atom showed a doublet of septets with $^2J_{P-H}$ = 473 Hz and $^3J_{H-H}$ = 5 Hz.

Compound **3c** was also characterized by ^1H NMR and single-crystal X-ray diffraction analyses. Although we were unable to locate and refine all the cluster hydrogen atoms, they were found from ^1H NMR study and the number of 4 was confirmed by integration of the signal against the signals of the PPr_3 ligands. An ORTEP diagram of the molecular structure of **3c** is shown in Figure 5. Selected bond distances and angles are listed in Table 4. Two distinct sets of Zr−Zr bond lengths again appear in this compound, Zr(P)−Zr(P) = 3.321(2) Å and Zr(P)−Zr(Cl) = 3.365(2) Å; both are slightly longer than those found in compounds **3a** and **3b**. Three different sets of bond lengths between Zr and bridging Cl atoms exist too: Zr(P)−Cl(ZrP,ZrP) = 2.564(4) Å, Zr(P)−Cl(ZrP,ZrCl) = 2.548(4) Å, and Zr(Cl)−Cl(ZrP,ZrCl) = 2.577(4) Å. The Zr−Clt distance is essentially the same as in compounds **3a** and **3b**, namely, 2.491(4) Å, and the average Zr to P bond length is 2.785(3) Å.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $Zr_6Cl_{14}(PPr_3)_4H_4\cdot 2.31C_6H_6$ (**3c**$\cdot 2.31C_6H_6$)[a]

Zr(1)−Zr(4)	3.314(2)	Zr(3)−Cl(1)	2.544(4)
Zr(1)−Zr(3)	3.326(2)	Zr(3)−Cl(7)	2.557(4)
Zr(1)−Zr(2)	3.361(2)	Zr(3)−Cl(10)	2.567(4)
Zr(1)−Zr(5)	3.369(2)	Zr(3)−Cl(11)	2.578(4)
Zr(2)−Zr(3)	3.364(2)	Zr(4)−Cl(6)	2.548(4)
Zr(2)−Zr(6)	3.365(2)	Zr(4)−Cl(12)	2.550(4)
Zr(2)−Zr(4)	3.372(2)	Zr(4)−Cl(2)	2.555(4)
Zr(3)−Zr(6)	3.318(2)	Zr(4)−Cl(8)	2.569(4)
Zr(3)−Zr(5)	3.359(2)	Zr(5)−Cl(14)	2.489(4)
Zr(4)−Zr(6)	3.326(2)	Zr(5)−Cl(12)	2.569(4)
Zr(4)−Zr(5)	3.366(2)	Zr(5)−Cl(7)	2.575(4)
Zr(5)−Zr(6)	3.368(2)	Zr(5)−Cl(4)	2.580(4)
Zr(1)−Cl(5)	2.551(4)	Zr(5)−Cl(9)	2.585(4)
Zr(1)−Cl(9)	2.553(4)	Zr(6)−Cl(3)	2.541(4)
Zr(1)−Cl(10)	2.558(3)	Zr(6)−Cl(4)	2.544(4)
Zr(1)−Cl(2)	2.561(4)	Zr(6)−Cl(8)	2.556(4)
Zr(2)−Cl(13)	2.494(4)	Zr(6)−Cl(11)	2.570(4)
Zr(2)−Cl(1)	2.569(4)	Zr(1)−P(2)	2.802(4)
Zr(2)−Cl(6)	2.574(4)	Zr(3)−P(1)	2.784(4)
Zr(2)−Cl(5)	2.580(4)	Zr(4)−P(4)	2.786(4)
Zr(2)−Cl(3)	2.582(4)	Zr(6)−P(3)	2.798(4)

Zr(4)−Zr(1)−Zr(3)	90.02(5)	Zr(1)−Zr(4)−Zr(5)	60.58(4)
Zr(2)−Zr(1)−Zr(5)	91.53(5)	Zr(6)−Zr(4)−Zr(5)	60.44(4)
Zr(1)−Zr(2)−Zr(6)	88.58(5)	Zr(1)−Zr(4)−Zr(2)	60.36(4)
Zr(3)−Zr(2)−Zr(4)	88.38(5)	Zr(6)−Zr(4)−Zr(2)	60.31(4)
Zr(6)−Zr(3)−Zr(1)	89.98(5)	Zr(3)−Zr(5)−Zr(6)	59.10(4)
Zr(5)−Zr(3)−Zr(2)	91.66(5)	Zr(4)−Zr(5)−Zr(6)	59.19(4)
Zr(1)−Zr(4)−Zr(6)	90.06(5)	Zr(3)−Zr(5)−Zr(1)	59.25(4)
Zr(5)−Zr(4)−Zr(2)	91.40(5)	Zr(4)−Zr(5)−Zr(1)	58.94(4)
Zr(3)−Zr(5)−Zr(4)	88.57(5)	Zr(3)−Zr(6)−Zr(2)	60.45(4)
Zr(6)−Zr(5)−Zr(1)	88.40(5)	Zr(4)−Zr(6)−Zr(2)	60.53(4)
Zr(3)−Zr(6)−Zr(4)	89.94(5)	Zr(3)−Zr(6)−Zr(5)	60.32(4)
Zr(2)−Zr(6)−Zr(5)	91.48(5)	Zr(4)−Zr(6)−Zr(5)	60.36(4)
Zr(4)−Zr(1)−Zr(2)	60.69(4)	Zr(3)−Cl(1)−Zr(2)	82.3(1)
Zr(3)−Zr(1)−Zr(2)	60.40(4)	Zr(4)−Cl(2)−Zr(1)	80.7(1)
Zr(4)−Zr(1)−Zr(5)	60.48(4)	Zr(6)−Cl(3)−Zr(2)	82.1(1)
Zr(3)−Zr(1)−Zr(5)	60.23(4)	Zr(6)−Cl(4)−Zr(5)	82.2(1)
Zr(1)−Zr(2)−Zr(3)	59.28(4)	Zr(1)−Cl(5)−Zr(2)	81.9(1)
Zr(3)−Zr(2)−Zr(6)	59.08(4)	Zr(4)−Cl(6)−Zr(2)	82.3(1)
Zr(1)−Zr(2)−Zr(4)	58.95(4)	Zr(3)−Cl(7)−Zr(5)	81.8(1)
Zr(6)−Zr(2)−Zr(4)	59.16(4)	Zr(6)−Cl(8)−Zr(4)	80.9(1)
Zr(6)−Zr(3)−Zr(5)	60.59(4)	Zr(1)−Cl(9)−Zr(5)	81.9(1)
Zr(1)−Zr(3)−Zr(5)	60.52(4)	Zr(1)−Cl(10)−Zr(3)	80.9(1)
Zr(6)−Zr(3)−Zr(2)	60.47(4)	Zr(6)−Cl(11)−Zr(3)	80.2(1)
Zr(1)−Zr(3)−Zr(2)	60.32(4)	Zr(4)−Cl(12)−Zr(5)	82.2(1)

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

A labeling experiment was carried out to verify that the hydrogen atoms found in the clusters $Zr_6Cl_{14}(PR_3)_4H_4$ (**3**) and $[Zr_6Cl_{18}H_5]^{3-}$ (**4**) and the cation $[HPR_3]^+$ are from the tin hydride reducing reagent, $HSnBu_3$. Reaction of brown solid **1** prepared by using $DSnBu_3$ and PPr_3 yielded $Zr_6Cl_{14}(PPr_3)_4D_4$ (**3c***) and $[DPPr_3]_3[Zr_6Cl_{18}D_5]$ (**4c***). ^1H NMR study showed no signals corresponding to the cluster hydrogen atoms or to the proton bonded directly to the phosphorus atom.

When the reaction of brown solid **1** with $P(t\text{-}Bu)_2Ph$ was carried out in CH_2Cl_2, the only product isolated from the resulting purple solution was $[HP(t\text{-}Bu)_2Ph]_3[Zr_6Cl_{18}H_5]$, **4d** (Scheme 3). Although the cation $[HP(t\text{-}Bu)_2Ph]^+$ might have been formed from the slow decomposition reaction of $Zr_6Cl_{14}(P(t\text{-}Bu)_2Ph)_4H_4$,[4] it is believed that the cation was more likely to have been formed by another mechanism because it was observed in a significant amount at the beginning of the reaction monitored by ^1H NMR spectroscopy. $[Zr_6Cl_{18}H_5]^{3-}$ (**4**) was the only hydrogen-containing cluster species present in the solution. Because of the enhanced solubility of [HP(*t*-

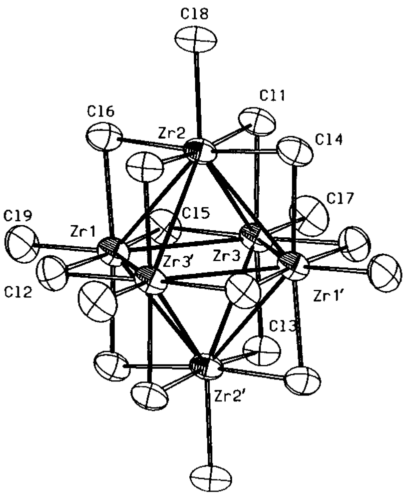
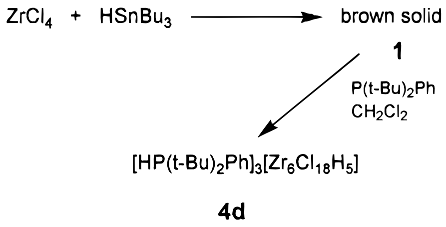


Figure 6. ORTEP drawing of the $[Zr_6Cl_{18}H_5]^{3-}$ cluster in the compound $[HP(t\text{-}Bu)_2Ph]_3[Zr_6Cl_{18}H_5]$ (**4d**) without cluster hydrogen atoms. Atoms are represented by their ellipsoids at the 50% probability level.

Scheme 3



Bu)$_2$Ph]Cl, there was a high concentration of Cl^- anions in solution, and these reacted with brown solid **1** to form $[Zr_6Cl_{18}H_5]^{3-}$ (**4**).[4] The very large cone angle (170°)[14] of $P(t\text{-}Bu)_2Ph$ does not favor the formation of $Zr_5Cl_{12}(PR_3)_5H_4$ (**2**) and $Zr_6Cl_{14}(PR_3)_4H_4$ (**3**) type clusters, which were not observed in this reaction. This supports our belief that $Zr_6Cl_{14}(PR_3)_4H_4$ (**3**) and $[Zr_6Cl_{18}H_5]^{3-}$ (**4**) are formed by different mechanisms from a common hexanuclear precursor in the brown solid **1**.

The cluster hydrogen atoms showed a slightly broad singlet signal at −3.03 ppm with an integrated intensity corresponding to five hydrogen atoms. Compound **4d** was also characterized by single-crystal X-ray diffraction analysis. An ORTEP diagram of the cluster anion $[Zr_6Cl_{18}H_5]^{3-}$ (**4**) is shown in Figure 6. Selected bond distances and angles are listed in Table 5. The six Zr atoms are arranged as an octahedron. The average Zr−Zr distance is 3.416(2) Å, which is significantly longer than those found in compounds **3a**−**c** of $Zr_6Cl_{14}(PR_3)_4H_4$ type clusters with four cluster hydrogen atoms. The bond length of a Zr atom to a terminal Cl atom is 2.486(4) Å, comparable to those in compounds **3a**−**c**, and the distance between a Zr atom and a bridging Cl atom is 2.577(4) Å, similar to the values of Zr(Cl)−Cl(ZrP,ZrCl) in a close coordination environment found in compounds **3a**−**c**.

Closing Remarks

Reduction of $ZrCl_4$ with the tin hydride reagent $HSnBu_3$ produces a brown solid, **1**. Although we have not been able to characterize brown solid **1** structurally, a series of pentanuclear ($Zr_5Cl_{12}(PR_3)_5H_4$ (**2**)) and hexanuclear ($Zr_6Cl_{14}(PR_3)_4H_4$ (**3**), $[Zr_6Cl_{18}H_5]^{3-}$ (**4**), and $[Zr_6Cl_{18}H_4]^{4-}$ (**5**)) hydrogen-containing cluster compounds have been isolated by solubilizing brown solid **1** with phosphines. The typical reaction and separation procedures are shown in Scheme 1. There may be two different kinds of precursors in brown solid **1**, leading to the formation of pentanuclear and hexanuclear compounds, respectively. By using the bulky phosphine $P(t\text{-}Bu)_2Ph$, only $[HP(t\text{-}Bu)_2Ph]_3[Zr_6Cl_{18}H_5]$ (**4d**) was observed and isolated. This suggests that $Zr_6Cl_{14}(PR_3)_4H_4$ (**3**) and $[Zr_6Cl_{18}H_5]^{3-}$ (**4**) are formed by different mechanisms, but probably from the same Zr_6 precursor in brown solid **1**. A deuterium-labeling experiment showed that the hydrogen atoms in $HSnBu_3$ are the source for the hydrogen atoms in $Zr_5Cl_{12}(PR_3)_5H_4$ (**2**), $Zr_6Cl_{14}(PR_3)_4H_4$ (**3**), and $[Zr_6Cl_{18}H_5]^{3-}$ (**4**) and the proton in $[HPR_3]^+$.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $[HP(t\text{-}Bu)_2Ph]_3[Zr_6Cl_{18}H_5]\cdot 2CH_2Cl_2\cdot 2C_6H_6$ ($\mathbf{4d}\cdot 2CH_2Cl_2\cdot 2C_6H_6$)[a]

Zr(1)−Zr(2)	3.413(2)	Zr(1)−Cl(5)	2.577(4)
Zr(1)−Zr(3)′	3.414(2)	Zr(1)−Cl(4)′	2.581(4)
Zr(1)−Zr(2)′	3.421(2)	Zr(2)−Cl(8)	2.496(4)
Zr(1)−Zr(3)	3.424(2)	Zr(2)−Cl(1)	2.567(4)
Zr(2)−Zr(3)	3.410(2)	Zr(2)−Cl(4)	2.567(4)
Zr(2)−Zr(3)′	3.415(2)	Zr(2)−Cl(6)	2.568(4)
Zr(2)−Zr(1)′	3.421(2)	Zr(2)−Cl(3)′	2.582(4)
Zr(3)−Zr(1)′	3.415(2)	Zr(3)−Cl(7)	2.491(4)
Zr(3)−Zr(2)′	3.415(2)	Zr(3)−Cl(2)′	2.565(4)
Zr(1)−Cl(9)	2.472(4)	Zr(3)−Cl(1)	2.571(4)
Zr(1)−Cl(2)	2.563(4)	Zr(3)−Cl(3)	2.573(4)
Zr(1)−Cl(6)	2.567(4)	Zr(3)−Cl(5)	2.581(4)
Zr(2)−Zr(1)−Zr(2)′	89.77(5)	Zr(3)−Zr(2)−Zr(1)′	59.99(4)
Zr(3)′−Zr(1)−Zr(3)	89.85(5)	Zr(3)′−Zr(2)−Zr(1)′	60.12(4)
Zr(3)−Zr(2)−Zr(3)′	90.08(5)	Zr(2)−Zr(3)−Zr(1)′	60.16(5)
Zr(1)−Zr(2)−Zr(1)′	90.23(5)	Zr(1)′−Zr(3)−Zr(2)′	59.97(4)
Zr(2)−Zr(3)−Zr(2)′	89.92(5)	Zr(2)−Zr(3)−Zr(1)	59.93(5)
Zr(1)′−Zr(3)−Zr(1)	90.15(5)	Zr(2)′−Zr(3)−Zr(1)	60.03(5)
Zr(2)−Zr(1)−Zr(3)′	60.02(4)	Zr(2)−Cl(1)−Zr(3)	83.2(1)
Zr(3)′−Zr(1)−Zr(2)′	59.85(4)	Zr(1)−Cl(2)−Zr(3)′	83.5(1)
Zr(2)−Zr(1)−Zr(3)	59.83(4)	Zr(3)−Cl(3)−Zr(2)′	83.0(1)
Zr(2)′−Zr(1)−Zr(3)	59.86(5)	Zr(2)−Cl(4)−Zr(1)′	83.3(1)
Zr(3)−Zr(2)−Zr(1)	60.24(4)	Zr(1)−Cl(5)−Zr(3)	83.2(1)
Zr(1)−Zr(2)−Zr(3)′	60.01(4)	Zr(1)−Cl(6)−Zr(2)	83.3(1)

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

We now begin to understand why different types of cluster compounds can be obtained from reactions under similar conditions, as reported before.[5,6] The compounds $Zr_6Cl_{14}(PR_3)_4H_4$ (**3a**, R = Me; **3b**, R = Et) are almost insoluble in benzene. Therefore, the pentanuclear compounds $Zr_5Cl_{12}(PR_3)_5H_4$ (**2a**, R = Me; **2b**, R = Et) were the only products isolated from the benzene solution.[5] The pentanuclear compounds **2** are only moderately stable in CH_2Cl_2 and very unstable in MeCN. This explains why only compounds **3** were obtained from the CH_2Cl_2 or MeCN solution.[6] By taking advantage of the differences in solubility and stability of different types of compounds, we have been successful in isolating all the different cluster products from the same reactions.

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Supporting Information Available: Full listings of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for compounds **3a**−**c** and **4d** (43 pages). Ordering information is given on any current masthead page.

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(14) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.