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Synthesis, Structure, and Reactivity of $[Zr_6Cl_{18}H_5]^{2-}$, the First Paramagnetic Species of Its Class

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Reaction of $[Zr_6Cl_{18}H_5]^{3-}$ (**1**) with 1 equiv of $TiCl_4$ yields a new cluster anion, $[Zr_6Cl_{18}H_5]^{2-}$ (**2**), which can be converted back into $[Zr_6Cl_{18}H_5]^{3-}$ (**1**) upon addition of 1 equiv of Na/Hg. Cluster **2** is paramagnetic and unstable in the presence of donor molecules. It undergoes a disproportionation reaction to form **1**, some Zr(IV) compounds, and H_2. It also reacts with $TiCl_4$ to form $[Zr_2Cl_9]^-$ (**4**) and a tetranuclear mixed-metal species, $[Zr_2Ti_2Cl_{16}]^{2-}$ (**3**). The oxidation reaction of **1** with $TiCl_4$ is unique. Oxidation of **1** with H^+ in CH_2Cl_2 solution results in the formation of $[ZrCl_6]^{2-}$ (**5**) and H_2, while in py solution the oxidation product is $[ZrCl_5(py)]^-$ (**6**). There is no reaction between **1** and TiI_4, $ZrCl_4$, $[TiCl_6]^{2-}$, $[ZrCl_6]^{2-}$, or $CrCl_3$. Compounds $[Ph_4P]_2[Zr_6Cl_{18}H_5]$ (**2a**), $[Ph_4P]_2[Zr_2Ti_2Cl_{16}]$ (**3a**), $[Ph_4P]_2[Zr_2Cl_9]$ (**4a**), $[Ph_4P]_2[ZrCl_6]\cdot 4MeCN$ (**5a**·4MeCN), and $[Ph_4P][ZrCl_5(py)]$ (**6a**) were characterized by X-ray crystallography. Compound **2a** crystallized in the trigonal space group $R\bar{3}$ with cell dimensions (20 °C) of $a = 28.546(3)$ Å, $b = 28.546(3)$ Å, $c = 27.679(2)$ Å, $V = 19533(3)$ Å^3, and $Z = 12$. Compound **3a** crystallized in the triclinic space group $P\bar{1}$ with cell dimensions (−60 °C) of $a = 11.375(3)$ Å, $b = 13.357(3)$ Å, $c = 11.336(3)$ Å, $\alpha = 106.07(1)°$, $\beta = 114.77(1)°$, $\gamma = 88.50(1)°$, $V = 1494.8(7)$ Å^3, and $Z = 1$. Compound **4a** crystallized in the triclinic space group $P\bar{1}$ with cell dimensions (−60 °C) of $a = 12.380(5)$ Å, $b = 12.883(5)$ Å, $c = 11.000(4)$ Å, $\alpha = 110.39(7)°$, $\beta = 98.29(7)°$, $\gamma = 73.12(4)°$, $V = 1572(1)$ Å^3, and $Z = 2$. Compound **5a**·4MeCN crystallized in the monoclinic space group $P2_1/c$ with cell dimensions (−60 °C) of $a = 9.595(1)$ Å, $b = 19.566(3)$ Å, $c = 15.049(1)$ Å, $\beta = 98.50(1)°$, $V = 2794.2(6)$ Å^3, and $Z = 2$. Compound **6a** crystallized in the monoclinic space group $P2_1/c$ with cell dimensions (20 °C) of $a = 10.3390(7)$ Å, $b = 16.491(2)$ Å, $c = 17.654(2)$ Å, $\beta = 91.542(6)°$, $V = 3026.4(5)$ Å^3, and $Z = 4$.

Introduction

A method to prepare new octahedral zirconium clusters, different from the "stuffed" ones pioneered by Corbett and coworkers,[1,2] has been developed in our laboratory. Reduction of $ZrCl_4$ with $HSn(n\text{-}Bu)_3$ followed by addition of Cl^- or phosphines has yielded a series of pentanuclear and hexanuclear zirconium cluster compounds containing two or more cluster hydrogen atoms.[3−9] These hydrogen-containing hexazirconium clusters ($[Zr_6Cl_{14}H_4(PR_3)_4]$,[7] $[Zr_6Cl_{18}H_5]^{3-}$,[6] $[Zr_6Cl_{18}H_4]^{4-}$,[9] and others) are different from the clusters formed in solid-state reactions in that they have no alien atoms at the center but instead have two to five hydrogen atoms in the clusters.

Even though so many hexazirconium clusters have been prepared and structurally characterized, their reactivities have scarcely been studied. With the Zr atoms in a low oxidation state and hydrogen atoms on the cluster, our hexazirconium clusters are potential reducing reagents. Reactions of the hexazirconium clusters with $TiCl_4$ and H^+ have yielded several new compounds, which are reported here.

Experimental Section

All manipulations were conducted under an argon atmosphere by using standard vacuum line and Schlenk technique. 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. $ZrCl_4$, $TiCl_4$, TiI_4, and $CrCl_3$ were purchased from Strem Chemicals and used as received. $[Ph_4P]Cl$, PMe_3, PMe_2Ph, Proton Sponge, and $(i\text{-}Pr)_2NLi$ were purchased from Aldrich. $[Ph_4P]Cl$ was dried at 150 °C under vacuum for 24 h. $[Ph_4P]_3[Zr_6Cl_{18}H_5]\cdot 3CH_2Cl_2$ (**1a**·$3CH_2Cl_2$),[6] $[Ph_4P]_4[Zr_6Cl_{18}H_4]\cdot 4MeCN$,[9] $[Ph_4P]_2[ZrCl_6]\cdot 2CH_2Cl_2$,[10] and $[MePPh_3]_2[TiCl_6]$[11] were prepared by the reported procedures. The ESR spectrum was recorded on a Brüker ESP 300 spectrometer at 100 K. The magnetic susceptibility was measured on a magnetic susceptibility balance from Johnson Matthey Chemicals Limited.

Preparation of $[Ph_4P]_2[Zr_6Cl_{18}H_5]$ (2a). A 200 mg (0.081 mmol) sample of $[Ph_4P]_3[Zr_6Cl_{18}H_5]\cdot 3CH_2Cl_2$ (**1a**·$3CH_2Cl_2$) was dissolved in 50 mL of CH_2Cl_2. To this purple solution was added dropwise 0.81 mL of 0.1 M $TiCl_4/CH_2Cl_2$ through a syringe. The solution turned blue instantly, and a brown precipitate was formed. The brown precipitate was separated from the solution by decantation. The blue solution was then evaporated to *ca.* 10 mL. Tiny cubic dark blue crystals of **2a** appeared within 30 min. After 12 h, the solution was decanted, and the crystalline yield of **2a** was 91% (138 mg). This reaction can be scaled up by a factor of 2−3. Attempts to grow crystals of the brown solid from its MeCN and Me_2CO solutions were unsuccessful.

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The ESR spectrum of **2a** in CH_2Cl_2 showed a broad signal with a *g* value of 1.978. Magnetic susceptibility for **2a**: $\chi = 1.10 \times 10^{-3}$ emu (295 K) after diamagnetic correction; $\mu_{eff} = 1.62\ \mu_B$ per cluster.

Crystals of **2a** suitable for single-crystal diffraction study were obtained by layering the blue solution with hexane. Cubic dark blue crystals appeared on the wall of the Schlenk tube within 3 days.

Reactions of $[Ph_4P]_3[Zr_6Cl_{18}H_5]$ (1a) with $[MePPh_3]_2[TiCl_6]$, TiI_4, $ZrCl_4$, $[Ph_4P]_2[ZrCl_6]$, and $CrCl_3$. No reaction between **1a** and up to 10 equiv of $[MePPh_3]_2[TiCl_6]$, TiI_4, $ZrCl_4$, $[Ph_4P]_2[ZrCl_6]$, or $CrCl_3$ was observed from studies in an NMR tube. There was no obvious change in the intensities of the cluster hydrogen signal in **1a** in 12 h.

Conversion of $[Ph_4P]_2[Zr_6Cl_{18}H_5]$ (2a) into $[Ph_4P]_3[Zr_6Cl_{18}H_5]$ (1a). A 200 mg (0.102 mmol) sample of **2a** was dissolved in 200 mL of CH_2Cl_2 and the solution was placed in a dry ice−acetone bath. Then 2.2 mL of 0.5 M Na/Hg was introduced into the solution with stirring. The color of the solution changed from blue to purple instantly. After 10 min, the dry ice−acetone bath was removed, and the solution was warmed up to room temperature. The purple solution was separated from the solid by decantation. The solution was reduced in vacuum to *ca.* 30 mL and then layered with 50 mL of hexane. Crystalline **1a**$\cdot 3CH_2Cl_2$ was isolated (138 mg, 55%). When this reaction was carried out in the presence of 1.0 equiv (0.102 mmol, 38 mg) of $[Ph_4P]Cl$, the isolated **1a**$\cdot 3CH_2Cl_2$ was 226 mg (90%).

Disproportionation of $[Ph_4P]_2[Zr_6Cl_{18}H_5]$ (2a). The blue color of compound **2a** in CH_2Cl_2 changed to purple with gas (presumably H_2) evolution upon addition of ligands, D: (D: = MeCN, Me_2CO, THF, py, PMe_3, and PMe_2Ph) possessing a lone pair of electrons. By layering of the purple solution with hexane, purple crystals of **1a**$\cdot 3CH_2Cl_2$, a white precipitate, and a small amount (*ca.* 5%) of colorless crystals of $[Ph_4P][Zr_2Cl_9]$ (**4a**) were isolated. Attempts to grow crystals from the white precipitate by using different ligands, D:, and different solvents failed. The isolated yields of compound **1a**$\cdot 3CH_2Cl_2$ from reaction of compound **2a** with 10 equiv of D: were 28% for MeCN, 25% for Me_2CO, 34% for THF, 20% for py, 29% for PMe_3, and 30% for PMe_2Ph. It is believed that ligands D: participated in the reactions because the yield of the product **1a**$\cdot 3CH_2Cl_2$ increased with the amount of D: used (up to 10 equiv) and the blue color of **2** vanished only after about 10 equiv of D: was added.

CH_2Cl_2 is the only solvent that we have found so far for compound **2a** that does not cause obvious decomposition during a short period of time. Even in CH_2Cl_2 solution, however, compound **2a** decomposed slowly. Within 2 weeks the distinguishing blue color of **2a** disappeared and a white precipitate was observed on the wall of the Schlenk tube. Layering the resulting purple solution with hexane allowed isolation of **1a**$\cdot 3CH_2Cl_2$ (24%) and **4a** (8%), as well as an amorphous white solid.

$$\underset{\mathbf{2a}}{[Ph_4P]_2[Zr_6Cl_{18}H_5]} \xrightarrow[\text{2 weeks}]{CH_2Cl_2} \underset{\mathbf{1a}}{[Ph_4P]_3[Zr_6Cl_{18}H_5]} + \underset{\mathbf{4a}}{[Ph_4P][Zr_2Cl_9]} + \text{white solid}$$

Reaction of $[Ph_4P]_2[Zr_6Cl_{18}H_5]$ (2a) with $TiCl_4$. A 4.2 mL aliquot of 0.1 M $TiCl_4/CH_2Cl_2$ was added slowly through a syringe to 100 mg (0.051 mmol) of **2a** in 100 mL of CH_2Cl_2 with stirring. The blue color of the solution changed to green with concomitant gas evolution (presumably H_2). After the volume of the solution was reduced to *ca.* 20 mL in vacuum, the solution was transferred to a Schlenk tube and layered with 40 mL of hexane. Then 35 mg (15%) of green crystals of $[Ph_4P]_2[Zr_2Ti_2Cl_{16}]$ (**3a**), 14 mg (11%) of colorless crystals of $[Ph_4P][Zr_2Cl_9]$ (**4a**), and an amorphous brown solid formed in 1 week. No crystals were obtained from the brown solid because of its insolubility. No intermediate products were isolated when a smaller amount of $TiCl_4$ was used either.

When the above reaction of **2a** and $TiCl_4$ was conducted in the presence of 480 mg (0.408 mmol) of $[Ph_4P]_2[ZrCl_6]\cdot 2CH_2Cl_2$, 223 mg (96%) of **3a** was isolated. Because crystals of both **4a** and $[Ph_4P]_2[ZrCl_6]\cdot 2CH_2Cl_2$ are colorless, they were not distinguishable from each other, and therefore it was impossible to determine the yield of **4a** in this reaction.

Reactions of $[Ph_4P]_3[Zr_6Cl_{18}H_5]$ (1a) with HCl, H_2O, and MeOH. Compound **1a**$\cdot 3CH_2Cl_2$ (100 mg, 0.041 mmol) was dissolved in 20 mL of CH_2Cl_2. To this solution was added 400 mL of 1.0 M of HCl/Et_2O. The purple color of the solution disappeared instantly, and an amorphous white precipitate was formed with gas (H_2) evolution. The white precipitate was insoluble in THF, MeCN, Me_2CO, CH_2Cl_2, and py. The colorless solution was layered with 30 mL of hexane. Colorless crystals of $[Ph_4P]_2[ZrCl_6]\cdot 2CH_2Cl_2$10 (63 mg, 22%) were obtained in 1 week. Use of less HCl resulted only in incomplete reaction and a lower yield of $[Ph_4P]_2[ZrCl_6]\cdot 2CH_2Cl_2$, but no intermediate products. Reaction of **1a** with 10 equiv of $MeOH/CH_2Cl_2$ was similar. The yield of $[Ph_4P]_2[ZrCl_6]\cdot 2CH_2Cl_2$ was 18% (52 mg).

When 100 mg (0.041 mmol) of **1a**$\cdot 3CH_2Cl_2$ in 20 mL of MeCN was treated with 400 mL of 1.0 M H_2O/MeCN, the change of solution color and bubbling were again observed. By layering of the resulting colorless solution with 2 mL of hexane and then 30 mL of Et_2O, 61 mg (22%) of colorless crystals of $[Ph_4P]_2[ZrCl_6]\cdot 4MeCN$ (**5a**$\cdot$4MeCN) was isolated in 10 days.

Reaction of 100 mg (0.041 mmol) of **1a**$\cdot 3CH_2Cl_2$ with 400 mL of 1.0 M H_2O/py proceeded similarly to the above reactions. By layering of the py solution with 30 mL of hexane, 70 mg (41%) of colorless crystals of $[Ph_4P][ZrCl_5(py)]$ (**6a**) were obtained in 1 week.

Reaction of $[Ph_4P]_3[Zr_6Cl_{18}H_5]$ (1a) with Proton Sponge. No reaction between **1a** and Proton Sponge (1,8-bis(dimethylamino)-naphthalene) was observed from a ^1H NMR study during a 12 h period of time.

Reaction of $[Ph_4P]_3[Zr_6Cl_{18}H_5]$ (1a) with (*i*-Pr)$_2$NLi. Compound **1a** in CH_2Cl_2 decomposed gradually upon addition of 1 equiv of (*i*-Pr)$_2$NLi to form a brown solid. Attempts to identify the brown solid by growing crystals were not successful because of its insolubility. No formation of $[Zr_6Cl_{18}H_4]^{4-}$ was observed during the reaction from ^1H NMR study.

Reaction of $[Ph_4P]_4[Zr_6Cl_{18}H_4]$ with H^+. No formation of $[Zr_6Cl_{18}H_5]^{3-}$ was observed during the reaction of $[Zr_6Cl_{18}H_4]^{4-}$ with 1 equiv of 1.0 M HCl/Et_2O in CD_2Cl_2 from ^1H NMR study. The reaction between $[Zr_6Cl_{18}H_4]^{4-}$ and 10 equiv of HCl/Et_2O was similar to that between **1** and H^+ described above with H_2 and $[Ph_4P]_2[ZrCl_6]\cdot 2CH_2Cl_2$ (*ca.* 25% yield) as products.

X-ray Crystallography

Diffraction intensity measurements at low temperature were made with crystals mounted on quartz fibers and placed in a cold stream of nitrogen. Crystals that were used at room temperature were mounted in thin-walled glass capillaries. Diffraction measurements were made on an Enraf-Nonius CAD4 automated diffractometer with graphite-monochromated Mo Kα radiation for compound **2a**, on a Rigaku AFC5R automated diffractometer with graphite-monochromated Cu Kα radiation for compound **6a**, and on an Enraf-Nonius FAST diffractometer with an area-detector and graphite-monochromated Mo Kα radiation for compounds **3a**, **4a**, and **5a**$\cdot$4MeCN. For the crystals on the CAD4 and Rigaku diffractometers, 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 provide all parameters and an orientation matrix. A total of 50 reflections were used in indexing and 250 reflections in cell refinement. Axial images were obtained to determine the Laue groups and cell dimensions. No decay corrections or absorption correction were applied.[12]

Each structure was solved by a combination of direct methods using the SHELXS-86 program[13a] and least-square refinement using SHELXL-93.[13b] Crystallographic data and results are listed in Table 1.

Compound **2a** crystallized in the rhombohedral crystal system. It was transformed into the *R*-centered trigonal cell. The Laue class $\bar{3}$

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Table 1. Crystal Data for Compounds **2a**, **3a**, **4a**, **5a**·4MeCN, and **6a**

	2a	**3a**	**4a**	**5a**·4MeCN	**6a**
formula	$C_{48}H_{46}Cl_{18}P_2Zr_6$	$C_{48}H_{40}Cl_{16}P_2Ti_2Zr_2$	$C_{24}H_{20}Cl_9PZr_2$	$C_{56}H_{52}Cl_6N_4P_2Zr$	$C_{29}H_{25}Cl_5NPZr$
fw	1870.21	1524.18	840.86	1146.88	686.94
cryst syst	trigonal	triclinic	triclinic	monoclinic	monoclinic
space group	$R\bar{3}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a, Å	28.546(3)	11.375(3)	12.380(5)	9.595(1)	10.3390(7)
b, Å	28.546(3)	13.357(3)	12.883(5)	19.566(3)	16.491(2)
c, Å	27.679(2)	11.336(3)	11.000(4)	15.049(1)	17.654(2)
α, (deg)	90	106.07(1)	110.39(7)	90	90
β, (deg)	90	114.77(1)	98.29(7)	98.50(1)	91.542(6)
γ, (deg)	120	88.50(1)	73.12(4)	90	90
V, $Å^3$	19533(3)	1494.8(7)	1572(1)	2794.2(6)	3026.4(5)
Z	12	1	2	2	4
d_{calc}, g/cm^3	1.906	1.693	1.777	1.363	1.508
μ, cm^{-1}	17.44	13.99	14.94	5.81	76.89
data collcn instrument	CAD-4	FR590	FR590	FR590	Rigaku
radiation (monochromated)	Mo Kα ($\lambda = 0.709\ 30$ Å)	Mo Kα ($\lambda = 0.709\ 30$ Å)	Mo Kα ($\lambda = 0.709\ 30$ Å)	Mo Kα ($\lambda = 0.709\ 30$ Å)	Cu Kα ($\lambda = 1.541\ 84$ Å)
temp, °C	20	−60	−60	−60	20
$2\theta_{max}$, deg	40	45	45	50	120
no. of observns ($I > 2\sigma(I)$)	4028	3718	3879	4818	4495
no. of variables	472	316	325	315	334
residuals: R1,[a] wR2[b]	0.050, 0.094	0.053, 0.120	0.050, 0.112	0.082, 0.145	0.067, 0.155
quality-of-fit indicator[c]	1.032	1.007	1.065	1.110	1.028
max shift in final cycle	−0.01	0	0	0	0
largest peak, e/$Å^3$	0.6((1)	0.7(1)	0.5(1)	0.73(9)	1.3(2)
abs cor	empirical	none	none	none	empirical

[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) $= [\sum[w(F_o^2 - F_c^2)^2]/(N_{observns} - N_{params})]^{1/2}$.

was identified from the lack of the *m* symmetry, and the space group $R\bar{3}$ (No. 148) was assumed and confirmed by successful solution and refinement of the structure. There are two independent $[Zr_6Cl_{18}H_5]^{2-}$ cluster anions in the unit cell, one located at an inversion center and the other on the $\bar{3}$ axis. All the non-hydrogen atoms were refined with anisotropic thermal parameters. Electron densities, which might be contributed from the cluster hydrogen atoms, were observed on or very close to the centers of the eight triangular faces of the Zr_6 octahedron. The positions of the hydrogen atoms in the $[Ph_4P]^+$ cations were calculated by assuming idealized geometry, C−H = 0.94 Å. Their positions were refined with fixed thermal parameters set at $1.2B_{eq}$ of the corresponding carbon atoms.

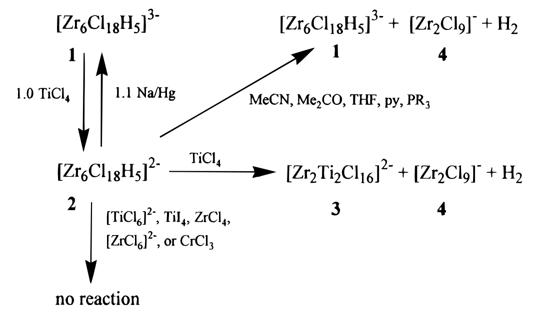
Compound **3a** crystallized in the triclinic crystal system. The space group $P\bar{1}$ (No. 2) was assumed and confirmed by successful solution and refinement of the structure. There are one $[Zr_2Ti_2Cl_{16}]^{2-}$ anion and two $[PPh_4]^+$ cations in the unit cell, and the $[Zr_2Ti_2Cl_{16}]^{2-}$ unit resides on an inversion center. All the non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms on the $[PPh_4]^+$ cations were calculated by assuming idealized geometry, C−H = 0.93 Å. They were refined with fixed thermal parameters set at 1.2 B_{eq} of the cooresponding carbon atoms.

Compound **4a** also crystallized in the triclinic crystal system. Again, the space group $P\bar{1}$ (No. 2) was assumed and confirmed by successful solution and refinement of the structure. There are two $[Zr_2Cl_9]^-$ anions and two $[Ph_4P]^+$ cations unit in the unit cell. All the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms on the phenyl rings were treated as in the previous compound.

Compound **5a**·4MeCN crystallized in the monoclinic crystal system. The space group $P2_1/c$ (No. 14) was identified uniquely from the systematic absence in the data. There are two $[ZrCl_6]^{2-}$ anions, four $[Ph_4P]^+$ cations, and eight MeCN solvent molecules in the unit cell. The $[ZrCl_6]^{2-}$ units are located at the inversion centers. All the non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were calculated by assuming idealized geometries with C−H = 0.93 Å for phenyl groups and C−H = 0.98 Å for methyl groups. They were refined with fixed thermal parameters of $1.2B_{eq}$ and $1.5B_{eq}$ for the corresponding carbon atoms, respectively.

Compound **6a** also crystallized in the monoclinic crystal system. The space group $P2_1/c$ (No. 14) was identified in the same way as described above. There are four $[ZrCl_5(py)]^-$ anions and four $[Ph_4P]^+$ cations in the unit cell. All the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were treated as in compound **2a**.

Scheme 1



Results and Discussion

The hydrogen-containing hexazirconium cluster $[Zr_6Cl_{18}H_5]^{3-}$ (**1**) is chemically reactive in general and could be a reducing species. The work reported here was undertaken to explore its reactivity with particular attention to its redox behaviors. For example, will a one-electron oxidation take place without significant structural change? Is it possible to remove one of the hydrogen atoms without rupturing the Zr_6 octahedron? And under what conditions will the cluster be broken?

The attempt to reduce $TiCl_4$ with 1 equiv of **1** resulted in the formation of a new and unexpected cluster species, $[Zr_6Cl_{18}H_5]^{2-}$ (**2**), in 91% yield (Scheme 1). The yellow $TiCl_4$ was reduced to form a brown solid. Because of the difficulties in separating it from the $[Zr_6Cl_{18}H_5]^{2-}$ compound, we have not yet been able to characterize the brown solid. The reaction is a one electron oxidation process and is reversible. By adding 1.1 equiv of Na/Hg to $[Ph_4P]_2[Zr_6Cl_{18}H_5]$ (**2a**) in the presence of 1.0 equiv of $[Ph_4P]Cl$, a 90% yield of $[Ph_4P]_3[Zr_6Cl_{18}H_5]$ (**1a**) was isolated. $[Ph_4P]Cl$ was needed in this reaction because the product **1a** has one more $[Ph_4P]^+$ cation than the starting material **2a**. Without addition of $[Ph_4P]Cl$, the yield of **1a** was only 55% based on Zr (but 82% based on $[Ph_4P]^+$). The

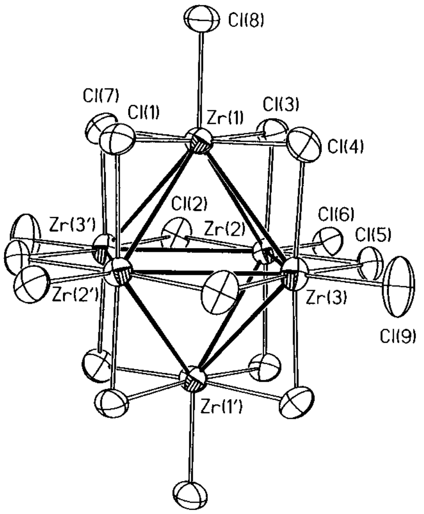


Figure 1. X-ray structure of one of the two independent $[Zr_6Cl_{18}H_5]^{2-}$ ions in $[Ph_4P]_2[Zr_6Cl_{18}H_5]$ (**2a**) showing 30% probability thermal ellipsoids of Zr and Cl atoms.

reactions were carried out in CH_2Cl_2, even though CH_2Cl_2 reacts with Na/Hg, because it is the only solvent we have found so far for compound **2a** in which it is moderately soluble and stable. Fortunately, at low temperature (−78 °C) the reaction between cluster **2** and Na/Hg is much faster than the reaction between CH_2Cl_2 and Na/Hg, and the yield of compound **1a** from compound **2a** was almost quantitative (90%). Since the interconversions between **1** and **2** are one-electron processes,**1** and **2** must contain the same number of hydrogen atoms, namely, 5. Cluster **2** has only 13 cluster-based electrons (CBE) with one unpaired electron in one of the bonding orbitals.[14] Its paramagnetism has been confirmed by an ESR spectrum and a magnetic susceptibility measurement. The ESR spectrum of compound **2a** showed a *g* value of 1.978, indicating the existence of an unpaired electron. The appearance of this signal indicates that the odd electron occupies a nondegenerate MO. From magnetic susceptibility measurement, the magnetic moment for each cluster is 1.62 μ_B, close to the value (1.73 μ_B) of spin-only magnetic moment for one unpaired electron.

Compound **2a** was also characterized by a single-crystal X-ray diffraction study. The molecular structure of the entire cluster anion, $[Zr_6Cl_{18}H_5]^{2-}$ is shown in Figure 1. Selected bond distances and angles are listed in Table 2. The structure of cluster **2** in compound **2a** is similar to that of **1**.[6] Six Zr atoms are arranged in an octahedron with six terminal and 12 edge-bridging Cl atoms. The average Zr−Zr distance is 3.459(2) Å, longer than that in $[Zr_6Cl_{18}H_5]^{3-}$, 3.407(1) Å.[6] Similar changes have been observed in other hexanuclear metal cluster systems, such $[Nb_6Cl_{18}]^{2-}$, $[Nb_6Cl_{18}]^{3-}$, and $[Nb_6Cl_{18}]^{4-}$,[15] as well as $[Ta_6Cl_{14}(PEt_3)_4]^+$ and $[Ta_6Cl_{14}(PEt_3)_4]$.[16] In contrast, the average bond lengths of $Zr-Cl_t$ (2.427(4) Å) and $Zr-Cl_b$ (2.557(4) Å) in cluster **2** are slightly shorter than those in cluster **1**, $Zr-Cl_t$ = 2.484(4) Å and $Zr-Cl_b$ = 2.568(4) Å.[6]

Surprisingly, the simple one-electron redox process between **1** and **2** could not be observed with cyclic voltammetry. A white film was formed and stuck firmly on the electrode surface. This might be the cause of failure to observe the expected reversible CV diagram.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2a**[a]

Zr(1)−Zr(3)′	3.451(2)	Zr(1)−Cl(1)	2.568(4)
Zr(1)−Zr(2)′	3.464(2)	Zr(2)−Cl(2)	2.551(4)
Zr(1)−Zr(2)	3.465(2)	Zr(2)−Cl(1)′	2.565(4)
Zr(2)−Zr(3)′	3.453(2)	Zr(2)−Cl(3)	2.569(4)
Zr(2)−Zr(3)	3.454(2)	Zr(2)−Cl(5)	2.571(4)
Zr(3)−Zr(1)′	3.451(2)	Zr(3)−Cl(4)	2.534(5)
Zr(11)−Zr(11)‴	3.442(3)	Zr(3)−Cl(2)′	2.552(4)
Zr(11)−Zr(11)′	3.442(3)	Zr(3)−Cl(7)′	2.560(4)
Zr(11)−Zr(11)″	3.489(3)	Zr(3)−Cl(5)	2.561(4)
Zr(2)−Cl(6)	2.436(4)	Zr(11)−Cl(13)	2.427(5)
Zr(1)−Cl(8)	2.430(4)	Zr(11)−Cl(11)	2.549(4)
Zr(3)−Cl(9)	2.414(5)	Zr(11)−Cl(12)	2.551(5)
Zr(1)−Cl(7)	2.545(4)	Zr(11)−Cl(12)′	2.556(5)
Zr(1)−Cl(4)	2.546(4)	Zr(11)−Cl(11)″	2.567(4)
Zr(1)−Cl(3)	2.557(4)		

Zr(3)′−Zr(1)−Zr(2)′	59.93(4)	Zr(1)′−Zr(2)−Zr(1)	90.16(5)
Zr(3)′−Zr(1)−Zr(2)	59.90(4)	Zr(2)′−Zr(3)−Zr(2)	90.20(5)
Zr(3)′−Zr(2)−Zr(1)′	60.12(5)	Zr(11)′−Zr(11)−Zr(11)″	90
Zr(3)−Zr(2)−Zr(1)′	59.86(4)	Zr(2)′−Cl(1)−Zr(1)	84.9(1)
Zr(3)′−Zr(2)−Zr(1)	59.86(4)	Zr(2)−Cl(2)−Zr(3)′	85.2(1)
Zr(3)−Zr(2)−Zr(1)	60.11(4)	Zr(1)−Cl(3)−Zr(2)	85.0(1)
Zr(1)′−Zr(3)−Zr(2)′	60.24(4)	Zr(3)−Cl(4)−Zr(1)	86.0(1)
Zr(1)′−Zr(3)−Zr(2)	60.22(4)	Zr(3)−Cl(5)−Zr(2)	84.6(1)
Zr(11)‴−Zr(11)−Zr(11)′	60.91(6)	Zr(1)−Cl(7)−Zr(3)′	85.1(1)
Zr(11)‴−Zr(11)−Zr(11)″	59.54(3)	Zr(11)−Cl(11)−Zr(11)′	86.0(1)
Zr(2)′−Zr(1)−Zr(2)	89.84(5)	Zr(11)−Cl(12)−Zr(11)‴	84.7(1)
Zr(3)′−Zr(2)−Zr(3)	89.80(5)		

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

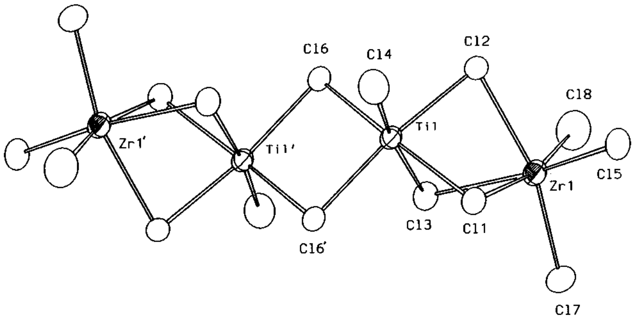


Figure 2. X-ray structure of $[Zr_2Ti_2Cl_{16}]^{2-}$ in $[Ph_4P]_2[Zr_2Ti_2Cl_{16}]$ (**3a**) showing 30% probability thermal ellipsoids.

Compound **2a** reacts further with $TiCl_4$. The distinguishing blue color vanished only after 8 equiv of $TiCl_4$ was added. Cluster hydrogen atoms were converted to H_2, which escaped from the solution during the reaction. Two new compounds, $[Ph_4P]_2[Zr_2Ti_2Cl_{16}]$ (**3a**) and $[Ph_4P][Zr_2Cl_9]$ (**4a**), were isolated in 15% and 11% yields, respectively (Scheme 1). Addition of less $TiCl_4$ resulted in lower yields of **3a** and **4a**. Disintegration of the cluster in **2a** into smaller units requires additional Cl ligands. When the reaction of **2a** with $TiCl_4$ was carried out in the presence of $[ZrCl_6]^{2-}$, the yield of **3a** increased to 96%. However, the mechanisms of the conversions of cluster **2** into $[Zr_2Ti_2Cl_{16}]^{2-}$ (**3**) and $[Zr_2Cl_9]^-$ (**4**) are not understood.

The structure of $[Zr_2Ti_2Cl_{16}]^{2-}$ is shown in Figure 2, and selected bond lengths and angles are listed in Table 3. The four metals are arranged in a nonlinear, centrosymmetric chain. The angle Zr(1)−Ti(1)−Ti(1)′ is 137.34(6)°. Clearly, two of the metal atoms are in oxidation state 4+, and the other two are in oxidation state 3+. Considering that Ti(IV) is much the easier to reduce, we propose to assign the Ti atoms as 3+. The distance between the two Ti atoms is 3.467(3) Å, longer than that between the Ti atom and the Zr atom, 3.429(2) Å. There is probably no metal−metal bond between the Ti atoms since the distance is longer than that in $[Ti_2(\mu\text{-}Cl)_3Cl_6]^{3-}$ (3.191 Å) which is without a Ti−Ti bond.[17] No compound containing a similar $Cl_4Ti^{III}(\mu\text{-}Cl)_2Ti^{III}Cl_4$ unit has been reported. The angle Ti(1)−Cl(6)−Ti(1)′ is 90.87°, close to the value 90° of the ideal

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(14) For MO diagrams of M_6 clusters, see: Lin, Z.; Williams, I. D. *Polyhedron* **1996**, *15*, 3277.

(15) Koknat, F. W.; McCarley, R. E. *Inorg. Chem.* **1974**, *13*, 295.

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for **3a**[a]

Zr(1)···Ti(1)	3.429(2)	Zr(1)−Cl(2)	2.601(2)
Ti(1)···Ti(1)′	3.467(3)	Ti(1)−Cl(4)	2.241(2)
Zr(1)−Cl(8)	2.341(2)	Ti(1)−Cl(6)′	2.431(2)
Zr(1)−Cl(5)	2.351(2)	Ti(1)−Cl(6)	2.435(2)
Zr(1)−Cl(7)	2.364(2)	Ti(1)−Cl(1)	2.479(2)
Zr(1)−Cl(3)	2.590(2)	Ti(1)−Cl(2)	2.480(2)
Zr(1)−Cl(1)	2.590(2)	Ti(1)−Cl(3)	2.511(2)
Zr(1)−Ti(1)−Ti(1)′	137.34(6)	Cl(4)−Ti(1)−Cl(6)	97.10(9)
Ti(1)−Cl(1)−Zr(1)	85.11(7)	Cl(6)′−Ti(1)−Cl(6)	89.13(8)
Ti(1)−Cl(2)−Zr(1)	84.85(7)	Cl(4)−Ti(1)−Cl(1)	92.20(9)
Ti(1)−Cl(3)−Zr(1)	84.48(6)	Cl(6)′−Ti(1)−Cl(1)	94.35(8)
Ti(1)′−Cl(6)−Ti(1)	90.87(8)	Cl(6)−Ti(1)−Cl(1)	169.66(9)
Cl(8)−Zr(1)−Cl(5)	97.13(9)	Cl(4)−Ti(1)−Cl(2)	95.08(9)
Cl(8)−Zr(1)−Cl(7)	97.87(9)	Cl(6)′−Ti(1)−Cl(2)	168.49(9)
Cl(5)−Zr(1)−Cl(7)	99.15(8)	Cl(6)−Ti(1)−Cl(2)	91.26(7)
Cl(8)−Zr(1)−Cl(3)	96.00(8)	Cl(1)−Ti(1)−Cl(2)	83.39(7)
Cl(5)−Zr(1)−Cl(3)	163.31(7)	Cl(4)−Ti(1)−Cl(3)	171.76(9)
Cl(7)−Zr(1)−Cl(3)	89.19(8)	Cl(6)′−Ti(1)−Cl(3)	88.15(8)
Cl(8)−Zr(1)−Cl(1)	167.41(8)	Cl(6)−Ti(1)−Cl(3)	89.89(8)
Cl(5)−Zr(1)−Cl(1)	88.15(7)	Cl(1)−Ti(1)−Cl(3)	80.51(7)
Cl(7)−Zr(1)−Cl(1)	92.53(8)	Cl(2)−Ti(1)−Cl(3)	80.35(7)
Cl(3)−Zr(1)−Cl(1)	77.00(6)	Cl(4)−Ti(1)−Zr(1)	123.24(8)
Cl(8)−Zr(1)−Cl(2)	89.35(8)	Cl(6)′−Ti(1)−Zr(1)	121.80(7)
Cl(5)−Zr(1)−Cl(2)	93.20(7)	Cl(6)−Ti(1)−Zr(1)	121.40(7)
Cl(7)−Zr(1)−Cl(2)	164.76(8)	Cl(1)−Ti(1)−Zr(1)	48.81(5)
Cl(3)−Zr(1)−Cl(2)	76.67(6)	Cl(2)−Ti(1)−Zr(1)	49.07(5)
Cl(1)−Zr(1)−Cl(2)	78.91(6)	Cl(3)−Ti(1)−Zr(1)	48.74(5)
Cl(8)−Zr(1)−Ti(1)	121.74(7)	Cl(4)−Ti(1)−Ti(1)′	99.41(8)
Cl(5)−Zr(1)−Ti(1)	116.87(6)	Cl(6)′−Ti(1)−Ti(1)′	44.60(5)
Cl(7)−Zr(1)−Ti(1)	119.37(7)	Cl(6)−Ti(1)−Ti(1)′	44.53(5)
Cl(3)−Zr(1)−Ti(1)	46.78(5)	Cl(1)−Ti(1)−Ti(1)′	138.08(8)
Cl(1)−Zr(1)−Ti(1)	46.08(5)	Cl(2)−Ti(1)−Ti(1)′	134.64(8)
Cl(2)−Zr(1)−Ti(1)	46.08(5)	Cl(3)−Ti(1)−Ti(1)′	88.62(7)
Cl(4)−Ti(1)−Cl(6)′	96.28(9)		

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

edge-sharing bioctahedron, consistent with there being no attraction between the two Ti atoms. Ti−Cl_t is shorter than Zr−Cl_t as expected, 2.241(2) *vs* 2.352(2) Å. The bond length between a Ti atom and the Cl atom bridging two Ti atoms is slightly shorter than that between a Ti atom and the Cl atom bridging a Ti atom and a Zr atom, Ti(1)−Cl(6) = 2.433(2) *vs* Ti(1)−Cl_b = 2.490(2) Å. However, both of them are significantly shorter than Zr(1)−Cl_b, 2.594(2) Å. The average of the Ti−Cl_b−Zr angles is 84.81(7)°, significantly larger than the value of 70.53° in the ideal face-sharing bioctahedron, indicating repulsion between the Zr and Ti atoms.

Although many phosphonium salts of $[Zr_2Cl_9]^-$ (**4a**) are known,[18] the structure of $[Zr_2Cl_9]^-$ has never been published. Compound $[Ph_4P][Zr_2Cl_9]$ (**4a**) was characterized by X-ray crystallography. The structure of **4a** is shown in Figure 3. The selected bond lengths and angles are listed in Table 4. The distance between the two Zr atoms is long, 3.562(3) Å. Zr−Cl_t = 2.336(3) Å, Zr−Cl_b = 2.576(3) Å, and the angle Zr−Cl_b−Zr = 87.4(1)°, all of which are consistent with a repulsive force between the Zr^{IV} atoms.

In the presence of ligands such as MeCN, Me_2CO, THF, py, and PR_3, cluster **2** disproportionates into **1** (in 20−34% yields), **4a** (*ca.* 5%) and a white solid, presumably a Zr(IV) compound since white is the typical color in amorphous form (Scheme 1). Cluster **2** is unstable even in CH_2Cl_2. Within 2 weeks, compound **2a** decomposed completely into **1a** (24%), and **4a** (8%), as well as an amorphous solid.

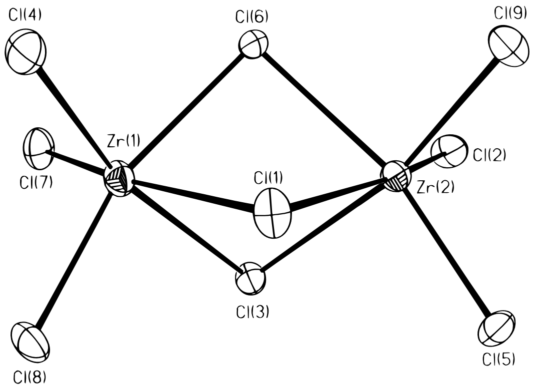


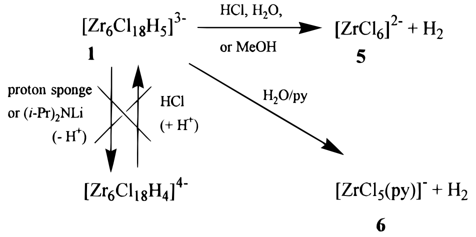
Figure 3. X-ray structure of $[Zr_2Cl_9]^-$ in $[Ph_4P][Zr_2Cl_{19}]$(**4a**) showing 30% probability thermal ellipsoids.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **4a**[a]

Zr(1)···Zr(2)	3.562(3)	Zr(1)−Cl(1)	2.562(2)
Zr(1)−Cl(4)	2.322(3)	Zr(1)−Cl(3)	2.580(3)
Zr(1)−Cl(7)	2.325(3)	Zr(1)−Cl(6)	2.580(2)
Zr(1)−Cl(8)	2.347(2)	Zr(2)−Cl(6)	2.573(3)
Zr(2)−Cl(5)	2.336(3)	Zr(2)−Cl(1)	2.578(2)
Zr(2)−Cl(9)	2.339(2)	Zr(2)−Cl(3)	2.585(2)
Zr(2)−Cl(2)	2.350(2)		
Zr(1)−Cl(1)−Zr(2)	87.7(1)	Zr(2)−Cl(6)−Zr(1)	87.45(9)
Zr(1)−Cl(3)−Zr(2)	87.20(8)		

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

Scheme 2



The reaction of **1** with $TiCl_4$ is unique. No reaction was found between **1** and $[TiCl_6]^{2-}$, nor does cluster **1** react with $[ZrCl_6]^{2-}$, TiI_4, $ZrCl_4$, or $CrCl_3$. The reactivity of $TiCl_4$ may be associated with the tendency of Ti^{III} to become 6-coordinated. It was expected that H^+ (from HCl, MeOH, or H_2O) might serve as a one-electron oxidant. In fact, reaction of **1** with H^+ led to the rupture of the Zr_6 cluster to form $[ZrCl_6]^{2-}$ in *ca.* 20% yield. Gas evolution (H_2) was observed during the reactions (Scheme 2). When the reaction was conducted in MeCN, a new crystalline form of $[Ph_4P]_2[ZrCl_6]$ (**5a**), **5a**·4MeCN was obtained. When the reaction was carried out in py, a new Zr(IV) compound ($[Ph_4P][ZrCl_5(py)]$ (**6a**)) was isolated.

The structure of $[ZrCl_6]^{2-}$ in $[Ph_4P]_2[ZrCl_6]$·4MeCN is shown in Figure 4. Selected bond lengths and angles are given in Table 5. The average Zr−Cl distance is 2.469(1) Å, close to those in other $[ZrCl_6]^{2-}$ compounds (2.463(8) Å in $[NEt_4]_2[ZrCl_6]$,[19a] 2.468(2) Å in $[(Et_2N)_3PCH_3]_2[ZrCl_6]$,[19b] and 2.463(1) Å in $[Ph_4P]_2[ZrCl_6]$·$2CH_2Cl_2$[10]). It is slightly longer than Zr−Cl_t in **2** (2.427(4) Å) and shorter than that in **1** (2.484(4) Å).[6]

The structure of the octahedral $[ZrCl_5(py)]^-$ (**6**) is shown in Figure 5. The average bond lengths and angles are given in Table 6. The py plane bisects angles Cl(5)−Zr(1)−Cl(1) and Cl(2)−Zr(1)−Cl(3). It is interesting to note that the Cl atoms

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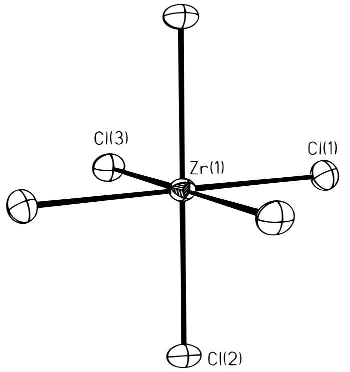

Figure 4. X-ray structure of $[ZrCl_6]^{2-}$ in $[Ph_4P]_2[ZrCl_6]$ (**5a**·4MeCN) showing 30% probability thermal ellipsoids.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **5a**·4MeCN[a]

Zr(1)−Cl(1)	2.473(1)	Zr(1)−Cl(3)	2.477(1)
Zr(1)−Cl(2)	2.458(1)		
Cl(2)′−Zr(1)−Cl(1)	89.77(5)	Cl(2)−Zr(1)−Cl(3)	90.44(4)
Cl(2)−Zr(1)−Cl(1)	90.23(5)	Cl(1)−Zr(1)−Cl(3)	89.43(5)
Cl(2)−Zr(1)−Cl(3)′	89.56(4)	Cl(1)′−Zr(1)−Cl(3)	90.57(5)
Cl(1)−Zr(1)−Cl(3)′	90.58(5)		

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

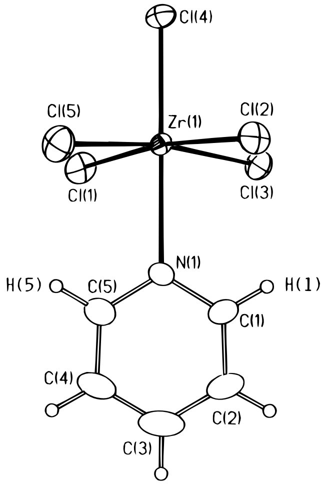

Figure 5. X-ray structure of $[ZrCl_5(py)]^-$ in $[Ph_4P][ZrCl_5(py)]$ (**6a**) showing 30% probability thermal ellipsoids.

at the equatorial positions (Cl(1), Cl(2), Cl(3), and Cl(5)) are all bent toward the py ligand. The average angle Cl(4)−Zr(1)−$Cl_{equatorial}$ is obviously larger than N(1)−Zr(1)−$Cl_{equatorial}$, 94.7(1)° *vs* 85.3(2)°. The driving force might be the existence of the hydrogen bonding between H(1) and H(5) on the py ligand and the equatorial Cl atoms, Cl···H = 3.21 Å.

In a previous paper,[9] we reported the synthesis and structure of $[Zr_6Cl_{18}H_4]^{4-}$. There are four hydrogen atoms in $[Zr_6Cl_{18}H_4]^{4-}$. The difference between $[Zr_6Cl_{18}H_4]^{4-}$ and **1** is only one H^+. But the addition of one H^+ to $[Zr_6Cl_{18}H_4]^{4-}$ to form **1** is not feasible. The addition resulted in decomposition of the Zr_6 cluster to form $[ZrCl_6]^{2-}$. Attempts to remove one H^+ from cluster **1** to form $[Zr_6Cl_{18}H_4]^{4-}$ with Proton Sponge and (*i*-Pr)$_2$NLi also failed.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **6a**[a]

Zr(1)−N(1)	2.405(8)	Zr(1)−Cl(5)	2.424(3)
Zr(1)−Cl(4)	2.398(2)	Zr(1)−Cl(2)	2.454(2)
Zr(1)−Cl(1)	2.422(2)	Zr(1)−Cl(3)	2.457(3)
Cl(4)−Zr(1)−N(1)	177.1(2)	Cl(1)−Zr(1)−Cl(3)	91.7(1)
Cl(1)−Zr(1)−Cl(2)	171.2(1)	N(1)−Zr(1)−Cl(1)	83.5(2)
Cl(5)−Zr(1)−Cl(3)	169.5(1)	N(1)−Zr(1)−Cl(5)	86.1(2)
Cl(4)−Zr(1)−Cl(1)	94.3(1)	N(1)−Zr(1)−Cl(2)	87.7(2)
Cl(4)−Zr(1)−Cl(5)	95.9(1)	Cl(5)−Zr(1)−Cl(2)	88.4(1)
Cl(1)−Zr(1)−Cl(5)	90.7(1)	N(1)−Zr(1)−Cl(3)	84.0(2)
Cl(4)−Zr(1)−Cl(2)	94.43(9)	Cl(2)−Zr(1)−Cl(3)	87.69(9)
Cl(4)−Zr(1)−Cl(3)	94.13(9)		

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

Conclusions

The hexazirconium clusters with main-group interstitial elements, obtained from solid-state reactions, generally contain the optimal, closed-shell complement of 14 cluster-based electrons (CBE).[1c,20] It is believed that the central atom and the electrons it could contribute to the bonding of the Zr_6 cluster are essential to the stabilization of the cluster.[2] It seems that the 14-electron rule also applies to the hydrogen-containing hexazirconium clusters: $[Zr_6Cl_{18}H_5]^{3-}$,[6] $[Zr_6Cl_{18}H_4]^{4-}$,[9] $[Zr_6Cl_{14}H_4(PR_3)_4]$,[7] $[Zr_6Cl_{12}H_2(PMe_2Ph)_6]$,[21] $[Zr_6Cl_{12}H_3(PEt_3)_6]^+$,[21] and $[Zr_6Cl_{13}H_3(PEt_3)_5]$.[21] It is difficult to oxidize $[Zr_6Cl_{18}H_5]^{3-}$ (**1**) to $[Zr_6Cl_{18}H_5]^{2-}$ (**2**), and the only reagent yet found to do this is $TiCl_4$. No reaction was found between **1** and $[TiCl_6]^{2-}$, TiI_4, $ZrCl_4$, $[ZrCl_6]^{2-}$, or $CrCl_3$. Reaction of **1** with H^+ led to decomposition of the Zr_6 cluster to form $[ZrCl_6]^{2-}$ and H_2. The cluster **2** is similar in structure to **1** with the five hydrogen atoms distributed over all eight triangular faces of the Zr_6 octahedron. However, the 13-electron cluster **2** is not stable in solution, where it disproportionates into the more stable 14-electron cluster **1**, $[Zr_2Cl_9]^-$, and H_2. Cluster **2** can be reduced and converted back into **1** almost quantitatively by reaction with 1 equiv of Na/Hg. However, the one-electron oxidation by $TiCl_4$ for **1** is not suitable for **2**. Reaction of **2** with $TiCl_4$ results in rupture of the Zr_6 cluster and formation of a new mixed-metal tetranuclear compound, $[Zr_2Ti_2Cl_{16}]^{2-}$ (**3**), $[Zr_2Cl_9]^-$, and H_2.

Although electron change has now been achieved in hydrogen-containing Zr_6 clusters by interconverting **1** and **2**, hydrogen atom change in these clusters has not as yet been achieved. Thus, while treatment of **1** with H^+ did not lead to $[Zr_6Cl_{18}H_4]^{2-} + H_2$, it is interesting that protonation, leading to $[Zr_6Cl_{18}H_6]^{2-}$, did not occur either. This may be compared with the fact that even though the difference between $[Zr_6Cl_{18}H_5]^{3-}$ and $[Zr_6Cl_{18}H_4]^{4-}$ is one H^+, and both of these exist, attempts to introduce one H^+ into $[Zr_6Cl_{18}H_4]^{4-}$ to form $[Zr_6Cl_{18}H_5]^{3-}$ or remove one H^+ from $[Zr_6Cl_{18}H_5]^{3-}$ with Proton Sponge or (*i*-Pr)$_2$NLi to form $[Zr_6Cl_{18}H_4]^{4-}$ have not succeeded.

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Supporting Information Available: An X-ray crystallographic file in CIF format is available on the internet. Access and ordering information is given on any current masthead page.

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