

Synthesis, Structure, and Reactivity of $[\text{Zr}_6\text{Cl}_{18}\text{H}_5]^{2-}$, the First Paramagnetic Species of Its Class

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Reaction of $[\text{Zr}_6\text{Cl}_{18}\text{H}_5]^{3-}$ (**1**) with 1 equiv of TiCl_4 yields a new cluster anion, $[\text{Zr}_6\text{Cl}_{18}\text{H}_5]^{2-}$ (**2**), which can be converted back into $[\text{Zr}_6\text{Cl}_{18}\text{H}_5]^{3-}$ (**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 $[\text{Zr}_2\text{Cl}_9]^-$ (**4**) and a tetranuclear mixed-metal species, $[\text{Zr}_2\text{Ti}_2\text{Cl}_{16}]^{2-}$ (**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 $[\text{ZrCl}_6]^{2-}$ (**5**) and H_2 , while in py solution the oxidation product is $[\text{ZrCl}_5(\text{py})]^-$ (**6**). There is no reaction between **1** and TiI_4 , ZrCl_4 , $[\text{TiCl}_6]^{2-}$, $[\text{ZrCl}_6]^{2-}$, or CrCl_3 . Compounds $[\text{Ph}_4\text{P}]_2[\text{Zr}_6\text{Cl}_{18}\text{H}_5]$ (**2a**), $[\text{Ph}_4\text{P}]_2[\text{Zr}_2\text{Ti}_2\text{Cl}_{16}]$ (**3a**), $[\text{Ph}_4\text{P}]_2[\text{Zr}_2\text{Cl}_9]$ (**4a**), $[\text{Ph}_4\text{P}]_2[\text{ZrCl}_6]\cdot 4\text{MeCN}$ (**5a**·4MeCN), and $[\text{Ph}_4\text{P}][\text{ZrCl}_5(\text{py})]$ (**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, $V = 19533(3)$ Å³, 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, $\alpha = 106.07(1)^\circ$, $\beta = 114.77(1)^\circ$, $\gamma = 88.50(1)^\circ$, $V = 1494.8(7)$ Å³, 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, $\alpha = 110.39(7)^\circ$, $\beta = 98.29(7)^\circ$, $\gamma = 73.12(4)^\circ$, $V = 1572(1)$ Å³, 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, $\beta = 98.50(1)^\circ$, $V = 2794.2(6)$ Å³, 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, $\beta = 91.542(6)^\circ$, $V = 3026.4(5)$ Å³, and $Z = 4$.

Introduction

A method to prepare new octahedral zirconium clusters, different from the “stuffed” ones pioneered by Corbett and co-workers,^{1,2} has been developed in our laboratory. Reduction of ZrCl_4 with $\text{HSn}(n\text{-Bu})_3$ 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 ($[\text{Zr}_6\text{Cl}_{14}\text{H}_4(\text{PR}_3)_4]$,⁷ $[\text{Zr}_6\text{Cl}_{18}\text{H}_5]^{3-}$,⁶ $[\text{Zr}_6\text{Cl}_{18}\text{H}_4]^{4-}$,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. $[\text{Ph}_4\text{P}]\text{Cl}$, PMe_3 , PMe_2Ph , Proton Sponge, and (*i*-Pr)₂NLi were purchased from Aldrich. $[\text{Ph}_4\text{P}]\text{Cl}$ was dried at 150 °C under vacuum for 24 h. $[\text{Ph}_4\text{P}]_3[\text{Zr}_6\text{Cl}_{18}\text{H}_5]\cdot 3\text{CH}_2\text{Cl}_2$ (**1a**·3CH₂Cl₂),⁶ $[\text{Ph}_4\text{P}]_4[\text{Zr}_6\text{Cl}_{18}\text{H}_4]\cdot 4\text{MeCN}$,⁹ $[\text{Ph}_4\text{P}]_2[\text{ZrCl}_6]\cdot 2\text{CH}_2\text{Cl}_2$,¹⁰ and $[\text{MePh}_3]_2[\text{TiCl}_6]$ ¹¹ were prepared by the reported procedures. The ESR spectrum was recorded on a Bruker ESP 300 spectrometer at 100 K. The magnetic susceptibility was measured on a magnetic susceptibility balance from Johnson Matthey Chemicals Limited.

Preparation of $[\text{Ph}_4\text{P}]_2[\text{Zr}_6\text{Cl}_{18}\text{H}_5]$ (2a**).** A 200 mg (0.081 mmol) sample of $[\text{Ph}_4\text{P}]_3[\text{Zr}_6\text{Cl}_{18}\text{H}_5]\cdot 3\text{CH}_2\text{Cl}_2$ (**1a**·3CH₂Cl₂) was dissolved in 50 mL of CH_2Cl_2 . To this purple solution was added dropwise 0.81 mL of 0.1 M $\text{TiCl}_4/\text{CH}_2\text{Cl}_2$ 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 Me₂CO solutions were unsuccessful.

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The ESR spectrum of **2a** in CH₂Cl₂ 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; $\mu_{\text{eff}} = 1.62 \mu_B$ per cluster.

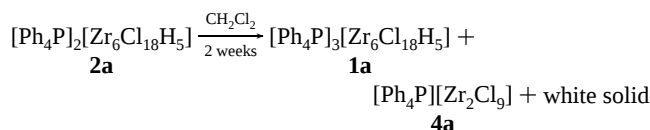
Crystals of **2a** suitable for single-crystal diffraction study were obtained by layering the blue solution with hexane. Cubic dark blue crystals appeared on the wall of the Schlenk tube within 3 days.

Reactions of [Ph₄P]₃[Zr₆Cl₁₈H₅] (1a) with [MePPh₃]₂[TiCl₆], TiCl₄, ZrCl₄, [Ph₄P]₂[ZrCl₆], and CrCl₃. No reaction between **1a** and up to 10 equiv of [MePPh₃]₂[TiCl₆], TiCl₄, ZrCl₄, [Ph₄P]₂[ZrCl₆], or CrCl₃ 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 [Ph₄P]₂[Zr₆Cl₁₈H₅] (2a) into [Ph₄P]₃[Zr₆Cl₁₈H₅] (1a). A 200 mg (0.102 mmol) sample of **2a** was dissolved in 200 mL of CH₂Cl₂ 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**·3CH₂Cl₂ was isolated (138 mg, 55%). When this reaction was carried out in the presence of 1.0 equiv (0.102 mmol, 38 mg) of [Ph₄P]Cl, the isolated **1a**·3CH₂Cl₂ was 226 mg (90%).

Disproportionation of [Ph₄P]₂[Zr₆Cl₁₈H₅] (2a). The blue color of compound **2a** in CH₂Cl₂ changed to purple with gas (presumably H₂) evolution upon addition of ligands, D: (D: = MeCN, Me₂CO, THF, py, PMe₃, and PMe₂Ph) possessing a lone pair of electrons. By layering of the purple solution with hexane, purple crystals of **1a**·3CH₂Cl₂, a white precipitate, and a small amount (ca. 5%) of colorless crystals of [Ph₄P][ZrCl₉] (**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**·3CH₂Cl₂ from reaction of compound **2a** with 10 equiv of D: were 28% for MeCN, 25% for Me₂CO, 34% for THF, 20% for py, 29% for PMe₃, and 30% for PMe₂Ph. It is believed that ligands D: participated in the reactions because the yield of the product **1a**·3CH₂Cl₂ 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.

CH₂Cl₂ 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 CH₂Cl₂ 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**·3CH₂Cl₂ (24%) and **4a** (8%), as well as an amorphous white solid.



Reaction of [Ph₄P]₂[Zr₆Cl₁₈H₅] (2a) with TiCl₄. A 4.2 mL aliquot of 0.1 M TiCl₄/CH₂Cl₂ was added slowly through a syringe to 100 mg (0.051 mmol) of **2a** in 100 mL of CH₂Cl₂ with stirring. The blue color of the solution changed to green with concomitant gas evolution (presumably H₂). 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 [Ph₄P]₂[Zr₂Ti₂Cl₁₆] (**3a**), 14 mg (11%) of colorless crystals of [Ph₄P][ZrCl₉] (**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 TiCl₄ was used either.

When the above reaction of **2a** and TiCl₄ was conducted in the presence of 480 mg (0.408 mmol) of [Ph₄P]₂[ZrCl₆]·2CH₂Cl₂, 223 mg (96%) of **3a** was isolated. Because crystals of both **4a** and [Ph₄P]₂[ZrCl₆]·2CH₂Cl₂ 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 [Ph₄P]₃[Zr₆Cl₁₈H₅] (1a) with HCl, H₂O, and MeOH. Compound **1a**·3CH₂Cl₂ (100 mg, 0.041 mmol) was dissolved in 20

mL of CH₂Cl₂. To this solution was added 400 mL of 1.0 M of HCl/Et₂O. The purple color of the solution disappeared instantly, and an amorphous white precipitate was formed with gas (H₂) evolution. The white precipitate was insoluble in THF, MeCN, Me₂CO, CH₂Cl₂, and py. The colorless solution was layered with 30 mL of hexane. Colorless crystals of [Ph₄P]₂[ZrCl₆]·2CH₂Cl₂ (63 mg, 22%) were obtained in 1 week. Use of less HCl resulted only in incomplete reaction and a lower yield of [Ph₄P]₂[ZrCl₆]·2CH₂Cl₂, but no intermediate products. Reaction of **1a** with 10 equiv of MeOH/CH₂Cl₂ was similar. The yield of [Ph₄P]₂[ZrCl₆]·2CH₂Cl₂ was 18% (52 mg).

When 100 mg (0.041 mmol) of **1a**·3CH₂Cl₂ in 20 mL of MeCN was treated with 400 mL of 1.0 M H₂O/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 Et₂O, 61 mg (22%) of colorless crystals of [Ph₄P]₂[ZrCl₆]·4MeCN (**5a**·4MeCN) was isolated in 10 days.

Reaction of 100 mg (0.041 mmol) of **1a**·3CH₂Cl₂ with 400 mL of 1.0 M H₂O/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 [Ph₄P][ZrCl₅(py)] (**6a**) were obtained in 1 week.

Reaction of [Ph₄P]₃[Zr₆Cl₁₈H₅] (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 [Ph₄P]₃[Zr₆Cl₁₈H₅] (1a) with (i-Pr)₂NLi. Compound **1a** in CH₂Cl₂ decomposed gradually upon addition of 1 equiv of (i-Pr)₂NLi to form a brown solid. Attempts to identify the brown solid by growing crystals were not successful because of its insolubility. No formation of [Zr₆Cl₁₈H₄]⁴⁻ was observed during the reaction from ¹H NMR study.

Reaction of [Ph₄P]₄[Zr₆Cl₁₈H₄] with H⁺. No formation of [Zr₆Cl₁₈H₅]³⁻ was observed during the reaction of [Zr₆Cl₁₈H₄]⁴⁻ with 1 equiv of 1.0 M HCl/Et₂O in CD₂Cl₂ from ¹H NMR study. The reaction between [Zr₆Cl₁₈H₄]⁴⁻ and 10 equiv of HCl/Et₂O was similar to that between **1** and H⁺ described above with H₂ and [Ph₄P]₂[ZrCl₆]·2CH₂Cl₂ (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 K α radiation for compound **2a**, on a Rigaku AFC5R automated diffractometer with graphite-monochromated Cu K α radiation for compound **6a**, and on an Enraf-Nonius FAST diffractometer with an area-detector and graphite-monochromated Mo K α radiation for compounds **3a**, **4a**, and **5a**·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 ₂ Zr ₆	C ₄₈ H ₄₀ Cl ₁₆ P ₂ Ti ₂ Zr ₂	C ₂₄ H ₂₀ Cl ₉ PZr ₂	C ₅₆ H ₅₂ Cl ₆ N ₄ P ₂ Zr	C ₂₉ H ₂₅ Cl ₅ NPZr
fw	1870.21	1524.18	840.86	1146.88	686.94
cryst syst	trigonal	triclinic	triclinic	monoclinic	monoclinic
space group	<i>R</i> 3̄	<i>P</i> 1̄	<i>P</i> 1̄	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	28.546(3)	11.375(3)	12.380(5)	9.595(1)	10.3390(7)
<i>b</i> , Å	28.546(3)	13.357(3)	12.883(5)	19.566(3)	16.491(2)
<i>c</i> , 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
<i>V</i> , Å ³	19533(3)	1494.8(7)	1572(1)	2794.2(6)	3026.4(5)
<i>Z</i>	12	1	2	2	4
<i>d</i> _{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 (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)	Cu Kα (λ = 1.541 84 Å)
temp, °C	20	-60	-60	-60	20
2θ _{max} , deg	40	45	45	50	120
no. of observns (<i>I</i> > 2σ(<i>I</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 = $[\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$; $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$ (also with $F_o^2 > 2\sigma(F_o^2)$). ^c Quality-of-fit (on F^2) = $[\sum [w(F_o^2 - F_c^2)^2] / (N_{\text{observns}} - N_{\text{params}})]^{1/2}$.

was identified from the lack of the *m* symmetry, and the space group *R*3̄ (No. 148) was assumed and confirmed by successful solution and refinement of the structure. There are two independent [Zr₆Cl₁₈H₅]²⁻ cluster anions in the unit cell, one located at an inversion center and the other on the 3̄ 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 Zr₆ octahedron. The positions of the hydrogen atoms in the [Ph₄P]⁺ cations were calculated by assuming idealized geometry, C-H = 0.94 Å. Their positions were refined with fixed thermal parameters set at 1.2*B*_{eq} of the corresponding carbon atoms.

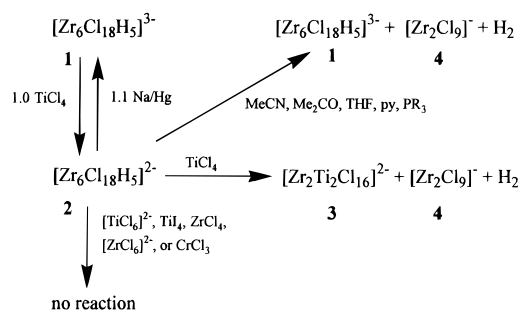
Compound **3a** crystallized in the triclinic crystal system. The space group *P*1̄ (No. 2) was assumed and confirmed by successful solution and refinement of the structure. There are one [Zr₂Ti₂Cl₁₆]²⁻ anion and two [PPh₄]⁺ cations in the unit cell, and the [Zr₂Ti₂Cl₁₆]²⁻ unit resides on an inversion center. All the non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms on the [PPh₄]⁺ 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 corresponding carbon atoms.

Compound **4a** also crystallized in the triclinic crystal system. Again, the space group *P*1̄ (No. 2) was assumed and confirmed by successful solution and refinement of the structure. There are two [Zr₂Cl₉]⁻ anions and two [Ph₄P]⁺ 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 *P*2₁/*c* (No. 14) was identified uniquely from the systematic absence in the data. There are two [ZrCl₆]²⁻ anions, four [Ph₄P]⁺ cations, and eight MeCN solvent molecules in the unit cell. The [ZrCl₆]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 1.2*B*_{eq} and 1.5*B*_{eq} for the corresponding carbon atoms, respectively.

Compound **6a** also crystallized in the monoclinic crystal system. The space group *P*2₁/*c* (No. 14) was identified in the same way as described above. There are four [ZrCl₅(py)]⁻ anions and four [Ph₄P]⁺ cations in the unit cell. All the non-hydrogen atoms were refined with

Scheme 1



anisotropic thermal parameters. The hydrogen atoms were treated as in compound **2a**.

Results and Discussion

The hydrogen-containing hexazirconium cluster [Zr₆Cl₁₈H₅]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 Zr₆ octahedron? And under what conditions will the cluster be broken?

The attempt to reduce TiCl₄ with 1 equiv of **1** resulted in the formation of a new and unexpected cluster species, [Zr₆Cl₁₈H₅]²⁻ (**2**), in 91% yield (Scheme 1). The yellow TiCl₄ was reduced to form a brown solid. Because of the difficulties in separating it from the [Zr₆Cl₁₈H₅]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 [Ph₄P]₂[Zr₆Cl₁₈H₅] (**2a**) in the presence of 1.0 equiv of [Ph₄P]Cl, a 90% yield of [Ph₄P]₃[Zr₆Cl₁₈H₅] (**1a**) was isolated. [Ph₄P]Cl was needed in this reaction because the product **1a** has one more [Ph₄P]⁺ cation than the starting material **2a**. Without addition of [Ph₄P]Cl, the yield of **1a** was only 55% based on Zr (but 82% based on [Ph₄P]⁺). The

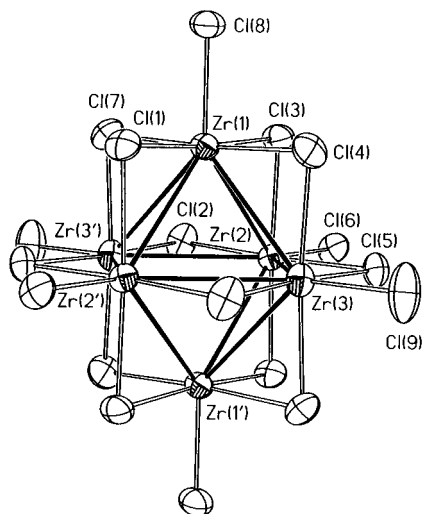


Figure 1. X-ray structure of one of the two independent [Zr₆Cl₁₈H₅]²⁻ ions in [Ph₄P]₂[Zr₆Cl₁₈H₅] (**2a**) showing 30% probability thermal ellipsoids of Zr and Cl atoms.

reactions were carried out in CH₂Cl₂, even though CH₂Cl₂ 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 CH₂Cl₂ 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, [Zr₆Cl₁₈H₅]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 [Zr₆Cl₁₈H₅]³⁻, 3.407(1) Å.⁶ Similar changes have been observed in other hexanuclear metal cluster systems, such [Nb₆Cl₁₈]²⁻, [Nb₆Cl₁₈]³⁻, and [Nb₆Cl₁₈]⁴⁻,¹⁵ as well as [Ta₆Cl₁₄(PEt₃)₄]⁺ and [Ta₆Cl₁₄(PEt₃)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.

Compound **2a** reacts further with TiCl₄. The distinguishing blue color vanished only after 8 equiv of TiCl₄ was added.

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.

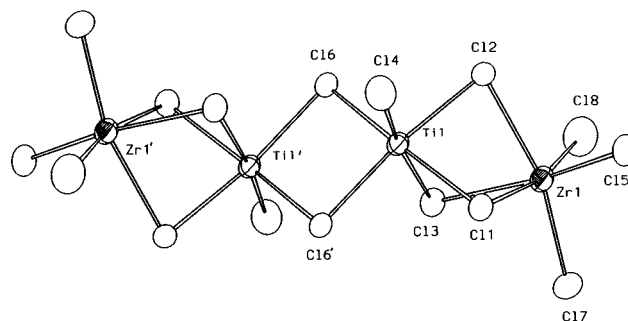


Figure 2. X-ray structure of [Zr₂Ti₂Cl₁₆]²⁻ in [Ph₄P]₂[Zr₂Ti₂Cl₁₆] (**3a**) showing 30% probability thermal ellipsoids.

Cluster hydrogen atoms were converted to H₂, which escaped from the solution during the reaction. Two new compounds, [Ph₄P]₂[Zr₂Ti₂Cl₁₆] (**3a**) and [Ph₄P][Zr₂Cl₉] (**4a**), were isolated in 15% and 11% yields, respectively (Scheme 1). Addition of less TiCl₄ 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 TiCl₄ was carried out in the presence of [ZrCl₆]²⁻, the yield of **3a** increased to 96%. However, the mechanisms of the conversions of cluster **2** into [Zr₂Ti₂Cl₁₆]²⁻ (**3**) and [Zr₂Cl₉]⁻ (**4**) are not understood.

The structure of [Zr₂Ti₂Cl₁₆]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 [Ti₂(μ-Cl)₃Cl₆]³⁻ (3.191 Å) which is without a Ti–Ti bond.¹⁷ No compound containing a similar Cl₄Ti^{III}(μ-Cl)₂Ti^{III}Cl₄ unit has been reported. The angle Ti(1)–Cl(6)–Ti(1)′ is 90.87°, close to the value 90° of the ideal

(14) For MO diagrams of M₆ clusters, see: Lin, Z.; Williams, I. D. *Polyhedron* **1996**, *15*, 3277.

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

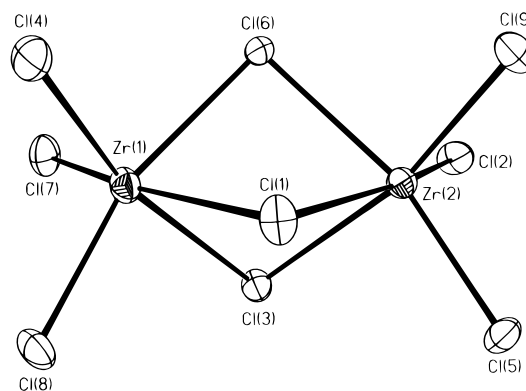
Zr(1)···Ti(1)	3.429(2)	Zr(1)—Cl(2)	2.601(2)
Ti(1)···Ti(1)'	3.467(3)	Ti(1)—Cl(4)	2.241(2)
Zr(1)—Cl(8)	2.341(2)	Ti(1)—Cl(6)'	2.431(2)
Zr(1)—Cl(5)	2.351(2)	Ti(1)—Cl(6)	2.435(2)
Zr(1)—Cl(7)	2.364(2)	Ti(1)—Cl(1)	2.479(2)
Zr(1)—Cl(3)	2.590(2)	Ti(1)—Cl(2)	2.480(2)
Zr(1)—Cl(1)	2.590(2)	Ti(1)—Cl(3)	2.511(2)
Zr(1)—Ti(1)—Ti(1)'	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 biotetrahedron, 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 biotetrahedron, indicating repulsion between the Zr and Ti atoms.

Although many phosphonium salts of [Zr₂Cl₉][−] (**4a**) are known,¹⁸ the structure of [Zr₂Cl₉][−] has never been published. Compound [Ph₄P][Zr₂Cl₉] (**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.

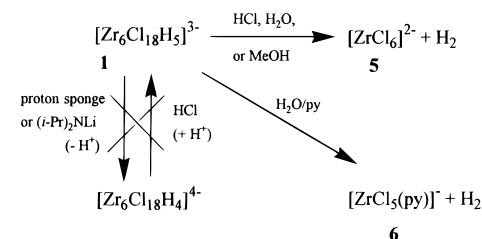
In the presence of ligands such as MeCN, Me₂CO, THF, py, and PR₃, cluster **2** disproportionates into **1** (in 20–34% yields), **4a** (*ca.* 5%) and a white solid, presumably a Zr(IV) compound since white is the typical color in amorphous form (Scheme 1). Cluster **2** is unstable even in CH₂Cl₂. Within 2 weeks, compound **2a** decomposed completely into **1a** (24%), and **4a** (8%), as well as an amorphous solid.

**Figure 3.** X-ray structure of [Zr₂Cl₉][−] in [Ph₄P][Zr₂Cl₉] (**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 TiCl₄ is unique. No reaction was found between **1** and [TiCl₆]^{2−}, nor does cluster **1** react with [ZrCl₆]^{2−}, TiI₄, ZrCl₄, or CrCl₃. The reactivity of TiCl₄ may be associated with the tendency of Ti^{III} to become 6-coordinated. It was expected that H⁺ (from HCl, MeOH, or H₂O) might serve as a one-electron oxidant. In fact, reaction of **1** with H⁺ led to the rupture of the Zr₆ cluster to form [ZrCl₆]^{2−} in *ca.* 20% yield. Gas evolution (H₂) was observed during the reactions (Scheme 2). When the reaction was conducted in MeCN, a new crystalline form of [Ph₄P]₂[ZrCl₆] (**5a**), **5a**·4MeCN was obtained. When the reaction was carried out in py, a new Zr(IV) compound ([Ph₄P][ZrCl₅(py)] (**6a**)) was isolated.

The structure of [ZrCl₆]^{2−} in [Ph₄P]₂[ZrCl₆]·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 [ZrCl₆]^{2−} compounds (2.463(8) Å in [NEt₄]₂[ZrCl₆],^{19a} 2.468(2) Å in [(Et₂N)₃PCH₃]₂[ZrCl₆],^{19b} and 2.463(1) Å in [Ph₄P]₂[ZrCl₆]·2CH₂Cl₂¹⁰). 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 [ZrCl₅(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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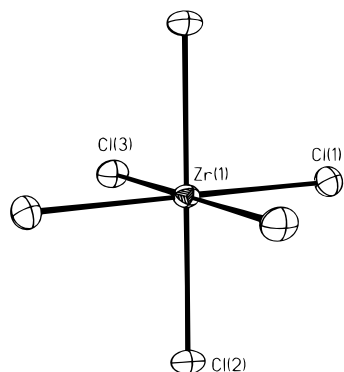


Figure 4. X-ray structure of [ZrCl₆]²⁻ in [Ph₄P]₂[ZrCl₆] (**5a**·4MeCN) showing 30% probability thermal ellipsoids.

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.

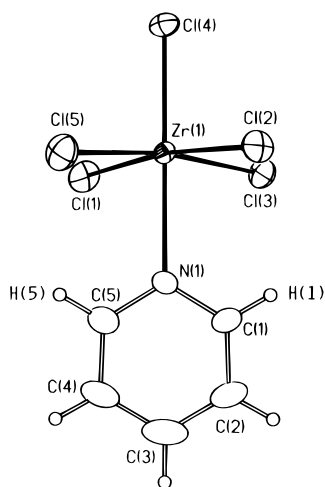


Figure 5. X-ray structure of [ZrCl₅(py)]⁻ in [Ph₄P][ZrCl₅(py)] (**6a**) showing 30% probability thermal ellipsoids.

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)^o vs 85.3(2)^o. 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 [Zr₆Cl₁₈H₄]⁴⁻. There are four hydrogen atoms in [Zr₆Cl₁₈H₄]⁴⁻. The difference between [Zr₆Cl₁₈H₄]⁴⁻ and **1** is only one H⁺. But the addition of one H⁺ to [Zr₆Cl₁₈H₄]⁴⁻ to form **1** is not feasible. The addition resulted in decomposition of the Zr₆ cluster to form [ZrCl₆]²⁻. Attempts to remove one H⁺ from cluster **1** to form [Zr₆Cl₁₈H₄]⁴⁻ with Proton Sponge and (*i*-Pr)₂NLi 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 Zr₆ 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: [Zr₆Cl₁₈H₅]³⁻,⁶ [Zr₆Cl₁₈H₄]⁴⁻,⁹ [Zr₆Cl₁₄H₄(PR₃)₄],⁷ [Zr₆Cl₁₂H₂(PMe₂Ph)₆],²¹ [Zr₆Cl₁₂H₃(PEt₃)₆]⁺,²¹ and [Zr₆Cl₁₃H₃(PEt₃)₅].²¹ It is difficult to oxidize [Zr₆Cl₁₈H₅]³⁻ (**1**) to [Zr₆Cl₁₈H₅]²⁻ (**2**), and the only reagent yet found to do this is TiCl₄. No reaction was found between **1** and [TiCl₆]²⁻, TiI₄, ZrCl₄, [ZrCl₆]²⁻, or CrCl₃. Reaction of **1** with H⁺ led to decomposition of the Zr₆ cluster to form [ZrCl₆]²⁻ and H₂. The cluster **2** is similar in structure to **1** with the five hydrogen atoms distributed over all eight triangular faces of the Zr₆ octahedron. However, the 13-electron cluster **2** is not stable in solution, where it disproportionates into the more stable 14-electron cluster **1**, [Zr₂Cl₉]⁻, and H₂. 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 TiCl₄ for **1** is not suitable for **2**. Reaction of **2** with TiCl₄ results in rupture of the Zr₆ cluster and formation of a new mixed-metal tetranuclear compound, [Zr₂Ti₂Cl₁₆]²⁻ (**3**), [Zr₂Cl₉]⁻, and H₂.

Although electron change has now been achieved in hydrogen-containing Zr₆ 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 [Zr₆Cl₁₈H₄]²⁻ + H₂, it is interesting that protonation, leading to [Zr₆Cl₁₈H₆]²⁻, did not occur either. This may be compared with the fact that even though the difference between [Zr₆Cl₁₈H₅]³⁻ and [Zr₆Cl₁₈H₄]⁴⁻ is one H⁺, and both of these exist, attempts to introduce one H⁺ into [Zr₆Cl₁₈H₄]⁴⁻ to form [Zr₆Cl₁₈H₅]³⁻ or remove one H⁺ from [Zr₆Cl₁₈H₅]³⁻ with Proton Sponge or (*i*-Pr)₂NLi to form [Zr₆Cl₁₈H₄]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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