

N-Centered Hexazirconium Chloride Clusters: Excision and Redox Chemistry

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The tightly cross-linked solid $Zr_6Cl_{15}N$ yields $[(Zr_6NCl_{12})Cl_6]^{3-}$ upon heating with bis(triphenylphosphine)iminium chloride (PPNCl), in MeCN at 90 °C. Purple solutions containing $[(Zr_6NCl_{12})Cl_6]^{3-}$ were obtained and characterized with ^{15}N NMR. Cyclic voltammetric (CV) measurements on the series of $[(Zr_6ZCl_{12})Cl_6]^{n-}$ cluster ions (Z = Be, B, C, and N) in acetonitrile reveal that these cluster ions exhibit multiple reversible redox waves at potentials that can be systematically understood, including a reversible redox wave corresponding to the $[(Zr_6NCl_{12})Cl_6]^{3-/4-}$ couple. Preparation of the reduced cluster ion, $[(Zr_6NCl_{12})Cl_6]^{4-}$, (with 15 cluster-bonding electrons) was achieved by reduction of $[(Zr_6NCl_{12})Cl_6]^{3-}$ with $(C_5(CH_3)_5)_2Co$. Several new N-centered cluster complexes: $(PPN)_3[(Zr_6NCl_{12})Cl_6] \cdot CH_2Cl_2$, $[(C_5(CH_3)_5)_2Co^+]_3[(Zr_6NCl_{12})Cl_6]$, and $(Et_4N)_4[(Zr_6NCl_{12})Cl_6] \cdot 2CH_3CN$ have been isolated and structurally characterized.

Introduction

The diverse chemistry of centered hexazirconium halide clusters $M^1_y[(Zr_6ZX_{12})X_m]$ (Z = H, Be–N, Al–P, Mn–Ni; X = Cl, Br, I; $0 \leq y, m \leq 6$) originated with solid-state synthetic and structural investigations in Corbett's laboratory.^{1–4} Hexazirconium cluster chemistry has been extended into solution via excision processes during which clusters are liberated from extended solid-state frameworks in precursors.^{5–10} Investigations of resulting discrete clusters in solution have provided us with a detailed understanding of their intrinsic properties and the prospect of using these cluster molecules to prepare new materials with tailored properties.

We have reported excision of Be-, B-, and C-centered hexazirconium halide clusters in polar solvents or ionic

liquids and our investigations of their corresponding solution chemistry.^{6,8–19} In this paper, we report the successful excision of an N-center cluster solid, $Zr_6Cl_{15}N$, and the isolation of N-centered hexazirconium chloride cluster complexes $(PPN)_3[(Zr_6NCl_{12})Cl_6] \cdot CH_2Cl_2$ (**1** and **2**) and $[(C_5(CH_3)_5)_2Co^+]_3[(Zr_6NCl_{12})Cl_6]$ (**3**) for the first time. We will also provide a systematic electrochemical investigation on the series of $[(Zr_6ZCl_{12})Cl_6]^{n-}$ (Z = Be, B, C, and N) clusters in MeCN, as well as the preparation of a one-electron-reduced cluster compound, $(Et_4N)_4[(Zr_6NCl_{12})Cl_6] \cdot 2CH_3CN$ (**4**).

Experimental Section

Techniques and Materials. All compounds were manipulated in a nitrogen-atmosphere glovebox or in Schlenk (Ar) or high-vacuum lines. The solid-state cluster precursor $Zr_6Cl_{15}^{15}N$ was synthesized by use of published procedures.²⁰ Syntheses of this and other cluster precursors were confirmed by Guinier X-ray powder diffraction. $ZrCl_4$ was sublimed four times prior to use. Zr powder

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is prepared from Zr foil by a hydrogenation–dehydrogenation process that has been described previously.³ $^{15}\text{N}\text{H}_4\text{Cl}$ (Isotec Inc.) and bis(pentamethylcyclopentadienyl)cobalt ($\text{Cp}^*\text{}_2\text{Co}$, Aldrich) powders were used as received. Tetraethylammonium tetrafluoroborate (Et_4NBF_4) was dried by azeotropic evaporation with acetonitrile (MeCN) three times before use. 1-Ethyl-3-methylimidazolium chloride (ImCl) was prepared and purified according to the literature method.²¹ Bis(triphenylphosphine)iminium chloride (PPNCl, Aldrich) was recrystallized three times from acetone with diethyl ether before use. Acetonitrile (MeCN, spectroscopic grade, Aldrich), dichloromethane (EM), and methanol (MeOH, EM) were dried by refluxing over phosphorus pentoxide, calcium hydride, and sodium methoxide overnight, respectively, and then distilling under nitrogen before use. Diethyl ether was dried over sodium metal and benzophenone and distilled under N_2 before use.

Preparation of $(\text{PPN})_3\text{Zr}_6\text{Cl}_{18}\text{N}$. A 140 mg portion of $\text{Zr}_6\text{Cl}_{15}^{15}\text{N}$ and 200 mg of PPNCl were loaded in an ampule, to which 6.0 mL of MeCN was added by use of a syringe. The ampule was then sealed under vacuum and placed into an oven at 90 °C for 30 h. After centrifugation, the deep purple solution was syringed into another ampule, and insoluble solid (~100 mg) was recycled. The purple solution was then dried on a Schlenk line, and the resulting purple solid was washed with three 3 mL aliquots of MeOH to remove excess PPNCl. Approximately 100 mg of purple residue, $(\text{PPN})_3\text{Zr}_6\text{Cl}_{18}^{15}\text{N}$, was dried on a Schlenk line and recovered (yield: 30%). Rod-shaped crystals of $(\text{PPN})_3[(\text{Zr}_6\text{NCl}_{12})\text{Cl}_6]\cdot\text{CH}_2\text{Cl}_2$ (**1**) and rhombic crystals of $(\text{PPN})_3[(\text{Zr}_6\text{NCl}_{12})\text{Cl}_6]\cdot 0.41\text{CH}_2\text{Cl}_2$ (**2**) were obtained by dissolving 2 mg of the purple solids in 0.5 mL of CH_2Cl_2 followed by layering with 1.0 mL of Et_2O .

Preparation of $(\text{Et}_4\text{N})_4[(\text{Zr}_6\text{NCl}_{12})\text{Cl}_6]\cdot 2\text{CH}_3\text{CN}$ (4**).** A 12 mg portion of $(\text{PPN})_3\text{Zr}_6\text{Cl}_{18}\text{N}$ (4.3 μmol), 7 mg of Et_4NBF_4 (32 μmol), and 5 mg of $\text{Cp}^*\text{}_2\text{Co}$ (15 μmol) were loaded into an ampule. Then, ~3.0 mL of doubly distilled MeCN was transferred into the ampule via vacuum distillation before the ampule was sealed with a torch. All reactants readily dissolved to generate a red-brown solution. The ampule was then opened in a glovebox, and ~1.5 mL of the solution was syringed into a long straight tube and a long U-shaped tube, respectively. A 2.0 mL volume of Et_2O was layered on top of the red solution in the straight tube, which was then sealed on the Schlenk line. Black crystals of **3** were formed after 2 days. The U tube, covered with a septum on its open end, was quickly evacuated on a Schlenk line before it was sealed with a torch. The empty arm was placed in a Dewar filled with water (slightly cooler than ambient by water evaporation). Upon slow evaporation of MeCN over a week, dark brown crystals of **4** were left at the dry end of the U tube.

NMR. ^{15}N solution NMR spectra were measured on a Varian Inova-400 broad-band spectrometer (at 40.523 MHz). A 10 mg portion of $(\text{PPN})_3\text{Zr}_6\text{Cl}_{18}\text{N}$ was dissolved in 0.3 mL of CD_2Cl_2 and 0.2 mL of CH_2Cl_2 to give a purple solution, and then, the solution was transferred to a 5-mm NMR tube. Chemical shifts for ^{15}N were measured using 90% formamide as external standard and set at $\delta = -268.05$ ppm versus neat liquid nitromethane. Pulses of 5 ms (~30°), acquisition times of 2 s, and delay times of 300 s were used; 220 transients were collected.

Electrochemical Studies. For each set of measurements, about 6 mL of MeCN solution of the species to be studied was transferred into an 8-mL five-neck flask. Each neck was covered by a septum; three of the necks are used to pass through electrodes, and when necessary, two necks allow for purging with N_2 gas. CV experi-

ments were carried out with a CH1620A electrochemical analyzer (HCH Instruments). A glassy carbon disk electrode served as a working electrode, the counter electrode was platinum wire, and the reference electrode was AgNO_3/Ag in 0.1 M $(\text{Bu}_4\text{N})\text{PF}_6$ MeCN solution. For the measurements of Be-, B-, and C-centered clusters, the concentrations were about 1.9, 1.9, and 1.6 mM, respectively, and ~0.20 M ImCl was used as the electrolyte; for the measurement of the N-centered cluster, the concentration was 2.8 mM, and 0.40 M $(\text{Et}_4\text{N})\text{BF}_4$ was used as the electrolyte.

X-ray Structure Determinations. Single-crystal structure determinations were undertaken on four compounds (**1–4**). In each case, immediately upon its removal from the mother solution, a crystal was coated with Apiezon-T stopcock grease, mounted on the tip of a glass fiber, and then inserted into the low-temperature nitrogen stream of the diffractometer for data collection. Data were collected at –163 °C for **1–3** and –113 °C for **4** using a Siemens (Bruker) SMART CCD (charge coupled device) equipped diffractometer with an LT-2 low-temperature apparatus. For all crystals, an entire sphere of data was collected using ω scans of 0.3° per frame for 30 s. A total of 1868 frames were collected with a maximum resolution of 0.75 Å. The first 50 frames were recollected at the end of data collection to check for decay. Cell parameters were retrieved using SMART software²² and refined on all observed reflections using SAINT software.²³ Data reduction was performed using SAINT, which corrects for Lorentz polarization and decay. A multiscan absorption correction was applied. Initial zirconium and chloride positions were obtained from SHELXS-93 direct methods output. Subsequently, the other non-hydrogen atomic positions were located directly from the electron-density difference maps. Structural refinements were performed on F^2 by the least-squares method using the SHELXL-97 package,²⁴ incorporated in SHELXTL-PC V5.03.²⁵ Idealized hydrogen positions on the organic cations were calculated and placed in the refinement with C–H distance equal to 0.94 Å. Structure refinements of **1**, **3**, and **4** proceeded routinely, and all non-hydrogen atoms in the unit cell were refined anisotropically. During the final stage of the structural refinement of **2**, an electron density residual in cavities proximal to an inversion center (Wyckoff site 4d) was modeled and refined such that each cavity was 41.1(7)% occupied with CH_2Cl_2 molecules in two equally probable orientations (related by the inversion center). An independent refinement on a second crystal showed the occupancy of this solvent site was variable. Thermal parameters for all non-hydrogen atoms, except disordered solvent molecule in **2**, were refined anisotropically. Pertinent crystallographic data for all compounds are summarized in Table 1; a thermal ellipsoid plot of the $(\text{Zr}_6\text{NCl}_{18})^{4-}$ ion in **4** is shown in Figure 1.

Results and Discussion

Dissolution of the $\text{Zr}_6\text{Cl}_{15}\text{N}$ Cluster Solids. Unlike other main-group-centered hexazirconium chloride cluster solids for which a diverse set of compositions and structures are known, only two compounds with N-centered clusters, $\text{Zr}_6\text{Cl}_{15}\text{N}$ or $\text{KZr}_6\text{Cl}_{15}\text{N}$, have been synthesized via solid-state

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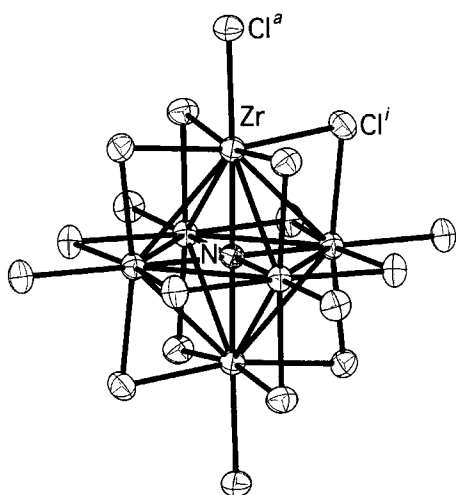
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Table 1. Crystallographic Data for N-Centered Zirconium Chloride Cluster Compounds

	1	2	3	4
formula	C ₁₀₈ H ₉₁ Cl ₂₀ N ₄ P ₆ Zr ₆	C _{108.4} H ₉₁ Cl _{18.8} N ₄ P ₆ Zr ₆	C ₆₀ H ₉₀ Cl ₁₈ Co ₃ NZr ₆	C ₃₆ H ₈₆ Cl ₁₈ N ₇ Zr ₆
fw, g/mol	2886.99	2848.24	2187.54	1802.54
space group	P1	C2/c	P1	P1
a, Å	14.6353(6)	33.1362(11)	13.0883(4)	12.2508(6)
b, Å	16.5553(7)	13.8161(4)	13.5359(4)	12.5219(6)
c, Å	27.2426(11)	28.3851(9)	13.7350(4)	12.9996(6)
α, deg	94.566(1)		65.989(1)	118.606(1)
β, deg	100.337(1)	116.882(2)	66.001(1)	93.528(1)
γ, deg	114.499(1)		69.577(1)	105.204(1)
V, Å ³	5820.8(4)	11590.8(6)	1980.93(10)	1647.76(14)
Z	2	4	1	1
ρ _{calcd} , g cm ⁻³	1.647	1.632	1.834	1.817
μ, mm ⁻¹	1.107	1.084	2.010	1.677
radiation (Mo, Å)	0.71073	0.71073	0.71073	0.71073
T, °C	-163.0	-163.0	-163.0	-113.0
R1, wR2 ^a (I > 2σ(I))	0.0507, 0.1239	0.0545, 0.1361	0.0494, 0.1164	0.0536, 0.1477
R1, wR2 (all data)	0.0787, 0.1401	0.1238, 0.1607	0.0634, 0.1273	0.0633, 0.1992

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{0.5}.$$

**Figure 1.** Structure of (Zr₆NCl₁₈)⁴⁻ (in 4), shown with 60% probability ellipsoids.

reactions.²⁰ No bromide- or iodide-supported analogues have been reported. This lack of structural and compositional diversity prevented us from developing the solution chemistry of N-centered cluster when our initial attempts at Zr₆Cl₁₅N dissolution failed. With a more comprehensive understanding of the cluster excision process, an improved protocol was tried, and excision of clusters from Zr₆Cl₁₅N was accomplished.

The phases Zr₆Cl₁₅N and Na₂Zr₆Cl₁₅B are isostructural with Ta₆Cl₁₅, in which every Ta₆Cl₁₂ cluster core shares all six terminal chlorides with neighboring clusters to form an extended 3D framework: (Ta₆Cl₁₂)Cl^{a-a}_{6/2}. Na₂Zr₆Cl₁₅B readily dissolves in MeCN to yield a solution containing discrete molecular clusters under ambient conditions; Zr₆-Cl₁₅N is entirely inert under identical conditions. On the basis of experience with many other systems, we attribute this difference in behavior to the difference in the strengths of Zr–Cl^{a-a} bonds in the two solid precursors: for Zr₆Cl₁₅N, *d*(Zr–Cl^{a-a}) = 2.594(3) Å, for Na₂Zr₆Cl₁₅B, *d*(Zr–Cl^{a-a}) = 2.681(6) Å.²⁶ The harsher conditions required for Zr₆Cl₁₅N dissolution are a consequence of the greater energy required

to break stronger intercluster linkages. We find that heating Zr₆Cl₁₅N with excess PPNCl in MeCN at 80–90 °C for 20–30 h is reasonably effective for promoting the excision of this solid precursor. We also observe that the (Zr₆NCl₁₂)³⁺ cluster core is not stable at elevated temperature in water and methanol. PPNCl, once dissolved in CH₃CN, provides excess chloride ions that serve as effective nucleophiles in the excision reaction; PPN⁺ is sufficiently robust to survive the excision conditions and serves as a counterion once discrete clusters are liberated from the solid framework.

A solution prepared by dissolution of (PPN)₃Zr₆Cl₁₈¹⁵N in CH₂Cl₂ exhibits a lone sharp resonance at δ = 247.9 ppm in the ¹⁵N NMR spectrum. We assigned this singlet to the cluster species [(Zr₆¹⁵NCl₁₂)Cl₆]³⁻. This chemical shift is consistent with our earlier ¹⁵N MAS solid-state NMR measurement on the precursor Zr₆Cl₁₅¹⁵N, which showed a resonance at 271 ppm.¹³ It should be noted that routine use of ¹⁵N NMR to study solution chemistry of the N-centered cluster is hampered by extremely long relaxation times (*T*₁) and lower sensitivity of this nucleus.

Electrochemical Studies. To understand electrochemical behavior of hexazirconium cluster compounds, familiarity with the electronic structures of these metal clusters is invaluable. Numerous molecular orbital calculations performed on a hexazirconium cluster indicate that the optimal electron count of cluster-based-electrons (CBEs) for a main-group-centered hexazirconium cluster is 14 electrons,^{3,27} which occupy seven molecular orbitals with a_{1g}, t_{1u}, and t_{2g} symmetries. According to this bonding picture, an electron is removed from the t_{2g} HOMO when a cluster with 14 CBEs is oxidized, while an electron is added to the a_{2u} LUMO as the cluster is reduced.

To reveal and systematize the redox properties of the main-group-centered hexazirconium chloride clusters, [(Zr₆ZCl₁₂)–Cl₆]ⁿ⁻ (Z = Be, B, C, N), and assess their reducing strength with respect to common redox reagents, we performed a series of cyclic voltammetric measurements on these cluster complexes in MeCN and dichloromethane; the results will be discussed in detail in each of the following sections. For

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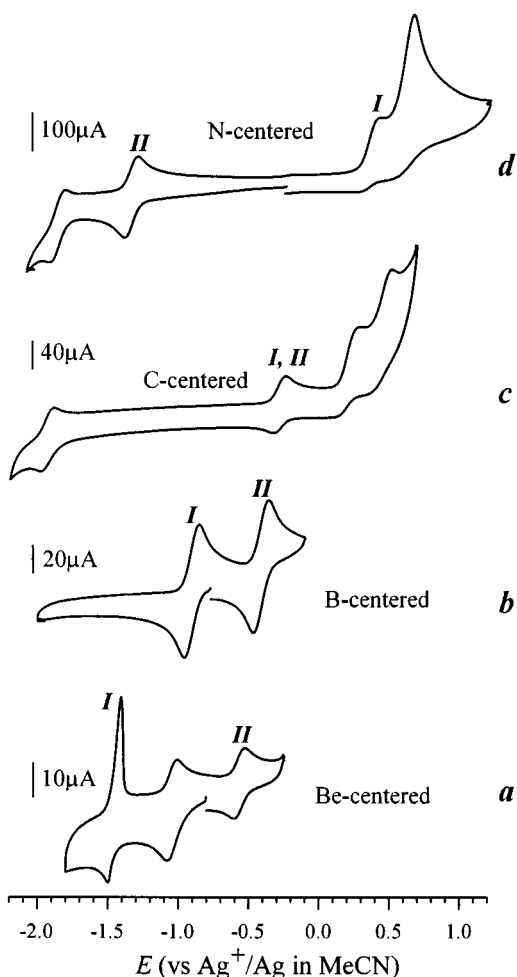


Figure 2. Cyclic voltammograms for MeCN solutions: (a) 1.9 mM $\text{Na}_4\text{Zr}_6\text{Cl}_{16}\text{Be}$ and 0.28 M ImCl; (b) 1.9 mM $\text{Im}_5\text{Zr}_6\text{Cl}_{18}\text{B}$ and 0.20 M ImCl; (c) 1.6 mM $\text{Im}_4\text{Zr}_6\text{Cl}_{18}\text{C}$ and 0.20 M ImCl; (d) 2.8 mM $(\text{PPN})_3\text{Zr}_6\text{Cl}_{18}\text{N}$ and 0.4 M $(\text{Et}_4\text{N})\text{BF}_4$. **I** labels redox waves corresponding to 13/14 CBE couples, and **II** labels redox waves corresponding to $[(\text{Zr}_6\text{ZCl}_{12})\text{Cl}_6]^{3-4-}$ ($Z = \text{Be}, \text{B}, \text{C}, \text{and N}$) couples.

the purposes of comparison, all voltammograms are overlaid in Figure 2, and important data associated with each redox wave are summarized in Table 2.

(a) $(\text{Zr}_6\text{BeCl}_{18})^{n-}$ Cluster Ions. The solid precursor $\text{Na}_4\text{Zr}_6\text{Cl}_{16}\text{Be}$ and 150 equiv ImCl readily dissolved in MeCN to yield a pink-red solution. Besides serving as the electrolyte for CV measurements, the excess ImCl is necessary to ensure that the fully chlorinated cluster, $(\text{Zr}_6\text{BeCl}_{18})^{n-}$, is the only major species in the solution. A cyclic voltammogram recorded for this solution is shown in Figure 2a. Three consecutive redox waves were clearly observed at -1.45 , -1.04 , and -0.56 V, which respectively correspond to $(\text{Zr}_6\text{BeCl}_{18})^{5-6-}$, $(\text{Zr}_6\text{BeCl}_{18})^{4-5-}$, and $(\text{Zr}_6\text{BeCl}_{18})^{3-4-}$ redox couples. The wave at -1.45 V displays an anomalous shape because deposition and stripping of $(\text{Zr}_6\text{BeCl}_{18})^{6-}$ cluster on the working electrode occurs. Consequently, the i_p^c/i_p^a ratio cannot be obtained. The $(\text{Zr}_6\text{BeCl}_{18})^{3-4-}$ (11/12 CBEs) redox couple was not observed in our previous electrochemical study in basic ImCl/ AlCl_3 ionic liquid;¹⁶ the i_p^c/i_p^a ratio (0.80) for this wave indicates that the cluster with 11 CBEs, a three-electron oxidation product, probably has marginal stability on the CV time scale. Preparatively, it has been observed

that oxidized (12 or 13 CBEs) Be-centered clusters, $(\text{Zr}_6\text{BeCl}_{18})^{4-5-}$, are stable and can be isolated in good yields.^{12,28} This electrochemical data also clearly show that $(\text{Zr}_6\text{BeCl}_{18})^{6-}$ cluster ion is a strong reducing agent ($E_{1/2} = -1.45$ V vs Ag^+/Ag in CH_3CN), and this is consistent with the difficulty we encounter when attempting to isolate $(\text{Zr}_6\text{BeCl}_{18})^{6-}$ from solution. The potential difference ($\Delta E_{1/2}$) between 13/14, 12/13 CBE couples and 12/13, 11/12 CBE couples are 0.41 and 0.48 V, respectively. This 0.4–0.5 V increment between consecutive $E_{1/2}$ values is similar to values measured for several series of hexazirconium halide ions in basic ImCl/ AlCl_3 and water.^{9,16}

(b) $(\text{Zr}_6\text{BCl}_{18})^{n-}$ Cluster Ions. A cyclic voltammogram recorded for an MeCN solution containing $(\text{Zr}_6\text{BCl}_{18})^{n-}$ cluster ions by dissolving $\text{Im}_5\text{Zr}_6\text{Cl}_{18}\text{B}$ and excess ImCl is shown in Figure 2b. Two well-defined redox waves at -0.903 and -0.410 V correspond to $(\text{Zr}_6\text{BCl}_{18})^{4-5-}$ and $(\text{Zr}_6\text{BCl}_{18})^{3-4-}$ redox couples, respectively. The ratios of peak currents associated with these two redox waves are close to unity, indicating that the cluster species generated by oxidation are stable on the time scale of the scans. The one-electron oxidized B-centered cluster, $\text{Im}_4\text{Zr}_6\text{BCl}_{18}$ (with 13 CBEs), can be prepared in good yield by chemically oxidizing $\text{Im}_5\text{Zr}_6\text{BCl}_{18}$ with $[\text{FeCp}_2]\text{BF}_4$ in basic $\text{AlCl}_3/\text{ImCl}$.¹⁹ Note that the ferrocenium salt appears to be a sufficiently strong oxidant in MeCN ($E^\circ = -0.04$ V vs Ag^+/Ag)²⁹ to oxidize the 14 CBE cluster, $(\text{Zr}_6\text{BCl}_{18})^{5-}$, by two electrons to produce $(\text{Zr}_6\text{BCl}_{18})^{3-}$ with 12 CBEs.

(c) $(\text{Zr}_6\text{CCl}_{18})^{n-}$ Cluster Ions. In the presence of excess ImCl, the C-centered 6–18 hexazirconium chloride cluster displays a single reversible wave at -0.29 V, corresponding to the $(\text{Zr}_6\text{CCl}_{18})^{3-4-}$ (13/14 CBEs) redox couple, as shown in Figure 2c. The large irreversible wave near $+0.28$ V indicates that the cluster species with 12 CBEs is not stable on the CV time scale. The large current observed at more positive potential signals cluster decomposition with likely formation of Zr^{IV} products. There is a clearly observable redox wave at -1.93 V that we attribute to the generation of a reduced C-centered cluster with 15 CBEs, though it is not particularly stable on the CV time scale. In our elementary molecular orbital interpretation of this $14 \rightarrow 15$ CBE couple, this is assigned as an $(a_{2u})^{0-1}$ configuration change, in which an electron enters a previously vacant orbital (a_{2u}) across the cluster HOMO–LUMO gap. We can estimate that this HOMO(t_{2g})–LUMO(a_{2u}) gap is ~ 1.2 eV by subtracting ~ 0.5 V, the value of $\Delta E_{1/2}$ observed for successive couples in the absence of any gap, from the potential difference ($\Delta E_{1/2} = 1.65$ V) between 13/14 and 14/15 CBE couples.

(d) $(\text{Zr}_6\text{NCl}_{18})^{n-}$ Cluster Ions. A cyclic voltammogram recorded for the purple solution prepared by dissolving $(\text{PPN})_3\text{Zr}_6\text{Cl}_{18}\text{N}$ in MeCN is shown in Figure 2d; the rest potential was found to be -0.25 V. Observation of an irreversible oxidation wave at ~ 0.36 V suggests that the N-centered cluster with 13 CBEs is unstable under these

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Table 2. Summary of Electrochemical Data for Main-Group-Centered Zirconium Chloride Clusters in MeCN Solution

	$E_{1/2}$, V	ΔE_p , V	i_p^c/i_p^a	$E_{1/2}$, V	ΔE_p , V	i_p^c/i_p^a	$E_{1/2}$, V	ΔE_p , V	i_p^c/i_p^a
[(Zr ₆ BeCl ₁₂)Cl ₆] in CH ₃ CN	-1.449	5 ⁻ /6 ⁻ , 13/14 CBEs	0.094	<i>a</i>	4 ⁻ /5 ⁻ , 12/13 CBEs	0.91 ^c	-0.562	3 ⁻ /4 ⁻ , 11/12 CBEs	0.80
[(Zr ₆ BCl ₁₂)Cl ₆] in CH ₃ CN				-0.903	4 ⁻ /5 ⁻ , 13/14 CBEs	0.96	-0.410	3 ⁻ /4 ⁻ , 12/13 CBEs	0.92
[(Zr ₆ CCl ₁₂)Cl ₆] in CH ₃ CN	0.28	2 ⁻ /3 ⁻ , 12/13 CBEs ^b	NA	NA	4 ⁻ /5 ⁻ , 14/15 CBEs	0.56 ^c	-0.287	3 ⁻ /4 ⁻ , 13/14 CBEs	0.90
[(Zr ₆ NCl ₁₂)Cl ₆] in CH ₃ CN	0.36	2 ⁻ /3 ⁻ , 13/14 CBEs ^b	NA	NA	4 ⁻ /5 ⁻ , 15/16 CBEs	0.10 ^c	-1.354	3 ⁻ /4 ⁻ , 14/15 CBEs	0.99 ^c
[(Zr ₆ NCl ₁₂)Cl ₆] in CH ₂ Cl ₂	0.279	2 ⁻ /3 ⁻ , 13/14 CBEs	0.126	0.69			-1.497	3 ⁻ /4 ⁻ , 14/15 CBEs	0.87

^a Redox wave associate with stripping and deposition of cluster species on the electrode. ^b Poorly defined oxidation wave that is onset of oxidative decomposition. ^c This is a reduction wave; the value of i_p^a/i_p^c is given.

conditions. On the other hand, at negative potential we find a well-defined redox wave at -1.35 V and a less-well behaved redox wave at -1.88 V. These two redox waves respectively correspond to (Zr₆NCl₁₈)^{3-/4-} and (Zr₆NCl₁₈)^{4-/5-} redox couples, which involve (a_{2u})⁰⁻¹ and (a_{2u})¹⁻² configuration changes. The i_p^a/i_p^c ratio of 0.99 for the (Zr₆NCl₁₈)^{3-/4-} redox couple suggested that the N-centered cluster with 15 CBEs might be preparatively accessible and motivated our use of Cp*₂Co to quantitatively convert (Zr₆NCl₁₈)³⁻ to (Zr₆NCl₁₈)⁴⁻ (see later). From the potential difference ($\Delta E_{1/2}$) of 1.72 V between 13/14 and 14/15 CBE redox couples, we estimate that the gap between a_{2u} and t_{2g} molecular orbitals is ~1.2 eV in the manner described previously.

A cyclic voltammogram recorded for a purple solution prepared by dissolving (PPN)₃Zr₆Cl₁₈N in CH₂Cl₂ displays two distinct redox waves at 0.279 and -1.497 V, which correspond to (Zr₆NCl₁₈)^{2-/3-} and (Zr₆NCl₁₈)^{3-/4-} redox couples, respectively. The redox wave associated with the (Zr₆NCl₁₈)^{2-/3-} (13/14 CBE) couple in CH₂Cl₂ displays a much-improved shape as compared with that in MeCN. The peak current ratio of 0.68 indicates a better stability of an N-centered cluster with 13 CBEs in CH₂Cl₂. Unfortunately, the potential of the 15/16 CBE redox couple is outside the CH₂Cl₂ electrochemical window.

(e) Electrochemical Correlations. Cluster ions with different interstitials exhibit different stabilities with respect to cluster decomposition upon oxidation or reduction. Oxidized Be-centered species, (Zr₆BeCl₁₈)^{3-/4-/5-} (11, 12, and 13 CBEs), all exhibit good stability in MeCN on the time scale of CV scans. In contrast, B-centered clusters with 11 CBEs, C-centered clusters with 11 or 12 CBEs, and N-centered clusters with 11, 12, or 13 CBEs are all unstable and decompose quickly in MeCN. Though there is no obvious explanation for it one notices that 6-18 cluster ions with core charges less than 3+, (Zr₆ZCl₁₂)^{m+} (Z = Be, B, C, N; $m \leq 3$), all exhibit reasonably good stability in MeCN, but if formed at all, 6-18 cluster ions with a (Zr₆ZCl₁₂)⁴⁺ core decompose rapidly to yield the simple Zr^{IV} products. The kinetic stability of hexazirconium clusters seems better correlated with the charge on the cluster than with the number of electrons involved in the metal cage bonding.

It is evident that cluster charge is closely correlated with reduction potential in MeCN. Reduction potentials ($E_{1/2}$'s) of species with the same charge change modestly on moving through the series Be → B → C, despite the different CBE

counts and interstitial atoms. For instance, $E_{1/2}$ for the (Zr₆ZCl₁₈)^{3-/4-} redox couple increases from -0.56 to -0.41 and to -0.29 V as Z changes from Be to B to C. These ~0.15 V shifts result from the increasing electronegativity of the interstitial (Z) as one traverses this series. Electrons in Zr-Z bonds are increasingly drawn toward the Z atom; this increases the positive charge on the Zr₆ cage making it more difficult to oxidize. Of course, the potentials observed in this series cannot extend to the N-centered case, for which one might naively expect to observe the (Zr₆NCl₁₈)^{3-/4-} redox couple at approximately -0.14 V. Instead, the (Zr₆NCl₁₈)^{3-/4-} couple is observed at a much more *negative* value ($E_{1/2} = -1.35$ V), because the oxidation of the (Zr₆NCl₁₈)⁴⁻ ion involves removal of an electron from the a_{2u} orbital that lies ~1.2 eV above a filled t_{2g} set. As we have indicated, we observe shifts of ~0.4-0.5 V in successive redox couples when the same or degenerate orbitals are involved. Shifts of this magnitude were also observed in our earlier electrochemical studies in basic AlCl₃/ImCl¹⁶ and aqueous solution.⁹

Chemical Reduction of [(Zr₆NCl₁₂)Cl₆]³⁻. Most hexazirconium cluster compounds obtained from solid-state syntheses have 14 CBEs, and among chloride compounds, very few with 13 or 15 CBEs are obtained from high-temperature reactions. The isolation of several oxidized cluster species with 13 or 12 CBEs was observed following excision of the cluster from solids.^{12,19,28} On the other hand, no reduced hexazirconium cluster complexes with 15 or 16 CBEs have ever been prepared and isolated from solution. Even when a solid with electron-rich clusters was used as a precursor, Zr₆I₂C (16 CBEs), a product with 14 CBE clusters, [(Zr₆-Cl₁₂)(H₂O)₆]₂, was isolated from the aqueous solution used in the excision process.¹⁰

The (Zr₆NCl₁₈)^{3-/4-} redox couple is associated with a nicely reversible redox wave with $E_{1/2} = -1.35$ V in MeCN, and we anticipated that bis(pentamethylcyclopentadienyl)-cobalt (Cp*₂Co; $E^\circ = -1.87$ V vs Ag⁺/Ag in CH₃CN)²⁹ would be sufficiently reducing to convert (Zr₆NCl₁₈)³⁻ to (Zr₆NCl₁₈)⁴⁻. Indeed, when (PPN)₃[(Zr₆NCl₁₂)Cl₆] was reacted with a slight excess of Et₄NBF₄ and Cp*₂Co in MeCN solution, the reduced cluster compound (Et₄N)₄[(Zr₆-NCl₁₂)Cl₆]·2CH₃CN (**4**) was isolated. Scrupulously dried MeCN and excess reducing agent are essential for the successful isolation of this 15 CBE cluster compound. With less careful handling, only the 14 CBE compound (Cp*₂-

Table 3. Selected Average Bond Lengths [Å] and Angles [deg] for **1–3, 4** and Related Hexazirconium Cluster Complexes

compound	CBEs	Zr–Z	Zr–Zr	Zr–Cl ⁱ	Zr–Cl ^a	<i>trans</i> -Cl ⁱ –Zr–Cl ⁱ	ref
Im ₃ [(Zr ₆ BCl ₁₂)Cl ₆]	14	2.3097(6)	3.266(1)	2.552(1)	2.637(3)		8
(Et ₄ N) ₄ [(Zr ₆ CCl ₁₂)Cl ₆]	14	2.2965(4)	3.2477(4)	2.5395(8)	2.5973(9)		28
1 , (PPN) ₃ [(Zr ₆ NCl ₁₂)Cl ₆]	14	2.2976(4)	3.2493(6)	2.521(1)	2.526(1)	170.18(4)	this work
3 , [Cp* ₂ Co] ₃ [(Zr ₆ NCl ₁₂)Cl ₆]							
4 , (Et ₄ N) ₄ [(Zr ₆ NCl ₁₂)Cl ₆]	15	2.2721(4)	3.2133(5)	2.542(1)	2.571(1)	168.33(4)	this work
(Et ₄ N) ₄ [(Zr ₆ CCl ₁₂)Cl ₆]	14	2.2965(4)	3.2477(4)	2.5395(8)	2.5973(9)		28
(Et ₄ N) ₄ [(Zr ₆ BCl ₁₂)Cl ₆]	13	2.361(1)	3.338(1)	2.567(2)	2.588(2)	171.1(1)	12
(Et ₄ N) ₄ [(Zr ₆ BeCl ₁₂)Cl ₆]	12	2.404(1)	3.399(2)	2.562(2)	2.568(2)		28

Co⁺)₃[(Zr₆NCl₁₂)Cl₆] (**3**) was isolated. Presumably, the reduced cluster was oxidized back to [(Zr₆NCl₁₂)Cl₆]³⁻ by traces of oxygen or moisture, which leaked into the reaction vessel during the handling, or such impurities consumed Cp*₂Co at the outset.

Crystal Structures. (PPN)₃[(Zr₆NCl₁₂)Cl₆]·CH₂Cl₂ (**1**) crystallizes in the triclinic space group *P* $\bar{1}$ with two clusters per unit cell. The nitrogen atom in one cluster resides at the origin of the unit cell, and the second cluster is centered on the center of the *bc* plane. The average Zr–Zr and Zr–N bond distances in **1** are, respectively, 3.2487(6) and 2.2972(4) Å. The [(Zr₆NCl₁₂)Cl₆]³⁻ cluster ions are surrounded by large PPN⁺ cations, all of which exhibit a bent conformation with an average P–N–P angle of 139.8(2)°. Compounds **2** and **1** are polymorphs; **2** crystallizes in the monoclinic space group *C2/c* with four clusters per unit cell. The nitrogen atom of the [(Zr₆NCl₁₂)Cl₆]³⁻ cluster sits on the 2-fold symmetry site (4e). One of the PPN⁺ ions has a linear P=N=P core and resides on an inversion center (4b); the other unique PPN⁺ ion displays a bent conformation with a P–N–P angle of 143.4(3)°. The average Zr–Zr and Zr–N bond distances in **2** are, respectively, 3.2466(7) and 2.295(4) Å. [(C₅(CH₃)₅)₂Co⁺]₃[(Zr₆NCl₁₂)Cl₆] (**3**) crystallizes in space group *P* $\bar{1}$ with one cluster per unit cell. The cluster sits at the origin of the unit cell, and one of the Cp*₂Co⁺ cations resides on the body center of the cell. The average Zr–Zr and Zr–N bond distances in **3** are, respectively, 3.2499(5) and 2.2980(4) Å, essentially identical with those in **1** and **2**. (Et₄N)₄[(Zr₆NCl₁₂)Cl₆]·2CH₃CN (**4**) is isotopic with the previously reported series of compounds (Et₄N)₄[(Zr₆ZCl₁₂)Cl₆]·2CH₃CN (Z = Be, B, and C).^{12,28} Compound **4** crystallizes in space group *P* $\bar{1}$ with one cluster per unit cell. Zr–Zr and Zr–N distances (3.2133(5) and 2.2721(4) Å, respectively) in **4** are somewhat shorter than corresponding distances in **1–3**. This shortening is consistent with the fact that the 15 CBE clusters have an additional electron in the a_{2u} SOMO that has weakly metal–metal bonding character.^{3,27,30,31} Similar, though more pronounced, shortening of the metal–metal bond distances were seen when (Nb₆Cl₁₂)⁴⁺ or (Ta₆Cl₁₂)⁴⁺ clusters (14 CBEs) were reduced to (Nb₆Cl₁₂)³⁺ or (Ta₆Cl₁₂)³⁺ (15 CBEs).^{32,33}

Structural Comparison of [(Zr₆ZCl₁₂)Cl₆]^{m-} (Z = Be, B, C, and N) Cluster Ions. The structural trends exhibited by the [(Zr₆ZCl₁₂)Cl₆]^{m-} (Z = Be, B, C, N) cluster family provide us with some clues about the properties or reactivity of these hexazirconium cluster molecules. Some structural comparisons of **1**, **3**, and **4** with previously reported cluster complexes are summarized in Table 3. It is interesting to compare the structural data of the series of [(Zr₆ZCl₁₂)Cl₆]^{m-} cluster ions in two ways: (i) comparing all cluster ions with 14 CBEs as interstitial species change from B, C, to N and (ii) comparing all cluster ions with a –4 charge over the range of interstitials (Be, B, C, N). Less complete, and less controlled, comparisons had been presented before on some solid-state cluster solids and a few molecular cluster complexes.^{19,20,34–39}

The cluster cores, (Zr₆ZCl₁₂)^{m+}, with 14 CBEs, display increasing positive charge (*m* = +1 → +2 → +3) as the interstitial changes from B → C → N. Consequently, the structural data (upper part of Table 3) reflect shrinking the interstitial size and the increasingly positive charge of the metal cage. The Zr₆C cage is noticeably smaller than the Zr₆B cage, but C- and N-centered cages have identical size. Metal–chloride bond distances (including Zr–Clⁱ and Zr–Cl^a bonds) decrease significantly with the increasing positive charge of (Zr₆Z)^{m+} cage. The (Zr₆NCl₁₂)³⁺ core has the greatest Lewis acidity: [(Zr₆NCl₁₂)Cl₆]³⁻ has short Zr–Cl^a bonds, and this is the only instance where Zr–Cl^a and Zr–Clⁱ bonds have comparable lengths. These short Zr–Cl^a bonds are consistent with our observation that terminal chlorides on N-centered cluster are less labile than those on Be- and B-centered clusters.

Let's consider cluster ions with the same charge (–4) while examining variations in the interstitial atom from Be to N. As we traverse the Be → N series, we are also increasing the number of bonding electrons (12 → 15 CBEs) in the Zr₆Z cage. The isotopic tetraethylammonium salts listed in Table 3 are particularly useful in making a controlled comparison. The structural data (bottom part of Table 3) clearly show that Zr–Z and Zr–Zr bond distances decrease significantly as the centered atom changes from Be → N. The decreasing size of the interstitial and the increasing population of the metal–metal bonding MOs are both contributing factors in this trend, but the latter seems to be

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most important. When the cluster-bonding electron (CBE) value changes from 14 to 15, the cluster contraction observed is smaller than the per-electron contractions observed on increasing the CBE count from 12 to 13 or from 13 to 14, in support of an argument that the a_{2u} orbital is more weakly metal–metal bonding MO than t_{2g} (by symmetry, neither orbital has significant Z-atom contributions).

Conclusions

For the first time, a solid with N-centered hexazirconium clusters, $Zr_6Cl_{15}N$, has successfully yielded discrete clusters, $[(Zr_6NCl_{12})Cl_6]^{3-}$. This is accomplished by heating $Zr_6Cl_{15}N$ and PPNCl in MeCN at 90 °C. Products with discrete cluster complexes, $(PPN)_3[(Zr_6NCl_{12})Cl_6]$, can be isolated and used as a precursor for solution chemistry of N-centered hexazirconium clusters. Data obtained from electrochemical measurements in MeCN solution reveal the redox properties of main-group-centered hexazirconium chloride cluster series: $[(Zr_6BeCl_{12})Cl_6]^{6-}$ (14 CBEs) and $[(Zr_6NCl_{12})Cl_6]^{4-}$ (15 CB-

Es) clusters are very strong one-electron reducing agents ($E_{1/2} = -1.41$ V and -1.31 V vs ferrocenium/ferrocene, respectively). One-electron chemical reduction of $[(Zr_6NCl_{12})Cl_6]^{3-}$ to $[(Zr_6NCl_{12})Cl_6]^{4-}$ was achieved by using Cp^*_2Co as a reducing agent, and the stable reduced cluster ion can be isolated quantitatively.

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Supporting Information Available: X-ray crystallographic file in CIF format for the structure determinations of $(PPN)_3[(Zr_6NCl_{12})Cl_6] \cdot CH_2Cl_2$ (**1**), $(PPN)_3[(Zr_6NCl_{12})Cl_6] \cdot 0.41CH_2Cl_2$ (**2**), $[(C_5(CH_3)_5)_2Co^+]_3[(Zr_6NCl_{12})Cl_6]$ (**3**), and $(Et_4N)_4[(Zr_6NCl_{12})Cl_6] \cdot CH_3CN$ (**4**). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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