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Articles

Isolation and Characterization of Bromination Products of $Zr(C_5H_5)_2Br_2$

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The reaction of $Zr(C_5H_5)_2Br_2$ with bromine can be used as an effective route to $Zr(C_5H_5)Br_3$. Through the slow addition of reactants, $Zr(C_5H_5)Br_3$ can be isolated in crystalline form. An X-ray diffraction study has revealed it to exist as a one-dimensional polymer, isomorphous with $Zr(C_5H_5)Cl_3$. In the presence of excess bromine, additional loss of C_5H_5 occurs, leading to the formation of the salt complex $[Zr_3(C_5H_5)_3Br_3(\mu_2\text{-}Br)_3(\mu_3\text{-}Br)_2]^+[Zr_2Br_9]^-$, as well as additional products. However, use of $Zr(C_5H_5)_2Br_2$ that has been exposed to air leads to traces of a water complex, $Zr_2(C_5H_5)_2Br_4(\mu_2\text{-}Br)_2(\mu_2\text{-}H_2O)$, which has been revealed through a structural study as having a confacial bioctahedral geometry, with the water serving as one of the three bridging ligands.

Introduction

While reliable synthetic routes to group IV $M(C_5H_5)_2X_2$ (X = halide) complexes have been long available,[1] that has not been the case for their $M(C_5H_5)X_3$ analogues. Nonetheless, various approaches have been developed for their syntheses,[2] or for adducts such as $Zr(C_5H_5)Cl_3(dme)$,[3] with the chlorination of $Zr(C_5H_5)_2Cl_2$ probably receiving the most attention.[4] However, even that approach can lead to contamination by tetrahalide impurities. Either these impurities can be removed by recrystallization[5] or their formation avoided by resorting to the bromination of $Zr(C_5H_5)_2Cl_2$,[6] leading to $Zr(C_5H_5)Cl_2Br$ (plus $C_5H_5Br_5$).[2,7] Although the mixed halide species $Zr(C_5H_5)Cl_2Br$ would be a suitable starting material for reactions in which all halides are to be replaced, in other situations one may run a risk of isolating compounds with both chloride and bromide ligands remaining, leading potentially to uncertain compositions and disordered structures. Hence, the bromination of $Zr(C_5H_5)_2Br_2$ to $Zr(C_5H_5)Br_3$ could become an advantageous alternative approach to mono(cyclopentadienyl)zirconium starting materials. Given that the structure of $Zr(C_5H_5)Br_3$ has not been reported, while that of $Zr(C_5H_5)Cl_3$ has been shown to be a one-dimensional, chloride-bridged polymer,[8] it was also of interest to determine whether the structures of these two species might be related. Herein we report details concerning the polymeric structure adopted by $Zr(C_5H_5)Br_3$, as well as the nature of an overhalogenation product, which is not simply a metal tetrahalide derivative, but rather an unusual salt composed of metal cluster ions. Additionally, oxygen-containing products have been isolated and characterized, reflecting the previously unappreciated favorability of water coordination by the hard Zr(IV) center in $Zr(C_5H_5)_2Br_2$.

Experimental Section

All reactions were carried out under a nitrogen atmosphere using Schlenk apparatus. THF was dried by distillation from sodium benzophenone ketyl under a nitrogen atmosphere, while other solvents were dried by activated alumina columns. $Zr(C_5H_5)_2Br_2$ was prepared by a published procedure[9] and stored in a glovebox when necessary to avoid the presence of oxygen-containing impurities. Elemental analyses were obtained from Desert Analytics and the microanalytical laboratories at the TU Braunschweig.

Tribromo(cyclopentadienyl)zirconium, $Zr(C_5H_5)Br_3$ (1). In a 250 mL Schlenk flask equipped with a dropping funnel, 1.89 g (4.96 mmol) of $Zr(C_5H_5)_2Br_2$ was dissolved in 50 mL of CH_2Cl_2. At −78°, 3.5 equiv of Br_2 (2.77 g, 0.89 mL) in 10 mL of CH_2Cl_2 was slowly added to the stirred solution over a period of 40 min. The resulting orange solution was warmed to room temperature, which led to a color change to red. After stirring overnight, a yellow precipitate was observable. The solids were separated with a frit

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[1] (a) Wilkinson, G.; Pauson, P. L.; Birmingham, J. M.; Cotton, F. A. *J. Am. Chem. Soc.* **1953**, *75*, 1011. (b) Summers, L.; Uloth, R. H. *J. Am. Chem. Soc.* **1954**, *76*, 2278. (c) Birmingham, J. M.; Seyferth, D.; Wilkinson, G. *J. Am. Chem. Soc.* **1954**, *76*, 4179. (d) Wilkinson, G.; Birmingham, J. M. *J. Am. Chem. Soc.* **1954**, *76*, 4281. (e) Summers, L.; Uloth, R. H.; Holmes, A. *J. Am. Chem. Soc.* **1955**, *77*, 3604.

[2] Gorsich, R. D. U.S. Patent 3,080,305, 1963.

[3] (a) Wells, N. J.; Huffman, J. C.; Caulton, K. G. *J. Organomet. Chem.* **1981**, *213*, C17. (b) Lund, E. C.; Livinghouse, T. *Organometallics* **1990**, *9*, 2426. (c) Hitchcock, P. B.; Lappert, M. F.; Liu, D.-S.; Ryan, E. J. *Polyhedron* **1995**, *14*, 2745. (d) Reid, A. F.; Wailes, P. C. *J. Organomet. Chem.* **1966**, *2*, 329. (e) Krebs, K. W.; Engelhard, H.; Nischk, G. E. *Chem. Abstr.* **1991**, *75*, 88768; Ger. Offen. 1,959,322, 1971.

[4] Erker, G.; Berg, K.; Sarter, C. *Organomet. Synth.* **1986**, *3*, 29.

[5] Casey, C. P.; Nief, F. *Organometallics* **1985**, *4*, 1218.

[6] Kulsomphob, V.; Harvey, B.; Arif, A. M.; Ernst, R. D. *Inorg. Chim. Acta* **2002**, *334*, 17.

[7] (a) Gorsich, R. D. *J. Am. Chem. Soc.* **1960**, *82*, 4211. (b) Zakharkin, L. I.; Orlova, L. V.; Lokshin, B. V.; Fedorov, L. A. *J. Organomet. Chem.* **1972**, *30*, 15. (c) Lucas, C. R.; Gabe, E. J.; Lee, F. L. *Can. J. Chem.* **1988**, *66*, 429. (d) Ernst, R. D.; Li, C.; Arif, A. M. *Z. Krist. NCS* **2005**, *220*, 279.

[8] Engelhardt, L. M.; Papasergio, R. I.; Raston, C. I.; White, A. H. *Organometallics* **1984**, *3*, 18.

[9] Druce, P. M.; Kingston, B. M.; Lappert, M. F.; Spalding, T. R.; Srivastava, R. C. *J. Chem. Soc. (A)* **1969**, 2106.

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from the yellowish solution and washed with 8 mL of CH_2Cl_2 to remove $C_5H_5Br_5$ and other impurities. After drying under high vacuum, 1.20 g (61%) of $Zr(C_5H_5)Br_3$ as a yellow powder was obtained. In a larger scale preparation, carried out with reagent and solvent quantities being 2.38 times those above (e.g., 4.51 g of $Zr(C_5H_5)_2Br_2$), and with a 60 min addition time, 3.39 g (72.5%) of product was obtained. Anal. Calcd for $C_5H_5ZrBr_3$: C, 15.16; H, 1.27. Found: C, 15.59; H, 1.67.

Crystallization of $Zr(C_5H_5)Br_3$ (1) and $Zr_2(C_5H_5)_2Br_4(\mu_2\text{-}Br)_2(\mu_2\text{-}H_2O)$ (3). Attempts to carry out the above reaction from more dilute solutions in the absence of stirring still led to powders, although occasionally over a period of 1–2 days, very small crystals of side products would form. In one such experiment 180. mg (0.472 mmol) of $Zr(C_5H_5)_2Br_2$ was dissolved in ca. 8 mL of CH_2Cl_2. The solution was cooled to −78 °C with dry ice, and 0.072 mL (1.43 mmol) of Br_2 was added with stirring. After 10 s the stirring was stopped, and the solution was allowed to warm slowly. One day later a significant quantity of powdered $Zr(C_5H_5)Br_3$ was observed, along with a small number of crystals. An X-ray structural determination revealed the crystals to be $Zr_2(C_5H_5)_2Br_4(\mu_2\text{-}Br)_2(H_2O)$. The source of the water was suspected to be the $Zr(C_5H_5)_2Br_2$, for which water coordination could be favored due to the hard nature of Zr(IV). This was supported by the acidic response shown by moist litmus paper in proximity to $Zr(C_5H_5)_2Br_2$ in a closed vial. For subsequent reactions, the $Zr(C_5H_5)_2Br_2$ starting material was stored in a glovebox, which then prevented the incorporation of water and oxygen-containing impurities.

Crystallization of $Zr(C_5H_5)Br_3$ was finally achieved by the following procedure. In a Schlenk tube, 120 mg (0.314 mmol) of $Zr(C_5H_5)_2Br_2$ was dissolved in ca. 4 mL of CH_2Cl_2. A shortened, narrow tube was placed into the Schlenk tube, and 0.056 mL (1.10 mmol) of Br_2 was syringed into the narrow tube. Subsequent gas phase diffusion of the bromine into the $Zr(C_5H_5)_2Br_2$ solution took place slowly enough that high-quality single crystals of the desired $Zr(C_5H_5)Br_3$ were formed.

$[Zr_3(C_5H_5)_3Br_3(\mu_2\text{-}Br)_3(\mu_3\text{-}Br)_2]^+[Zr_2Br_9]^-$ (2). A 156 mg (0.409 mmol) portion of $Zr(C_5H_5)_2Br_2$ was dissolved in 5 mL of freshly distilled CH_2Cl_2 at 0 °C in a 100 mL Schlenk flask equipped with a rubber septum. Eight equivalents (0.168 mL, 3.27 mmol) of deoxygenated bromine was added by syringe. The mixture was stirred very briefly to bring about complete mixing, after which it was left to sit undisturbed. After about 1 h, nicely formed yellow crystals were observed to have deposited. After one day, the supernatant was removed and 92 mg (38%) of the product was obtained. More dilute solutions of $Zr(C_5H_5)_2Br_2$ can be used, which increases the time for crystal growth. However, on some occasions crystalline products were not obtained from the dilute solutions. Use of excess bromine was often found to promote the formation and/or crystallization of this product from such dilute solutions of $Zr(C_5H_5)_2Br_2$. The X-ray structural determination revealed that the complex crystallizes with 2 equiv of CH_2Cl_2 in the lattice. Anal. Calcd for $C_{15}H_{15}Br_{17}Zr_5$: C, 8.96; H, 0.75. Calcd for $C_{15}H_{15}Br_{17}Zr_5 \cdot 2CH_2Cl_2$: C, 9.37; H, 0.87. Found: C, 9.04; H, 1.18.

X-Ray Diffraction Studies. Single crystals of each compound were obtained as described above, mounted on glass fibers with Paratone oil, and transferred to an Enraf-Nonius Kappa CCD diffractometer for data collection and unit cell determination. Initial structural solutions were obtained via direct methods using SIR 97, and subsequently any remaining atoms were located from difference Fourier maps using SHELXL97, which also was used for final structure refinements. For the $Zr(C_5H_5)Br_3$ and $Zr_2(C_5H_5)_2(Br)_6(H_2O)$ structures, all non-hydrogen atoms were refined anisotropically, while carbon-bound hydrogen atoms were assigned isotropic thermal parameters and allowed to ride on their attached atoms. The two hydrogen atoms of the coordinated water molecule were located from a difference Fourier map and subjected to constrained positional refinement, with the O−H distance set to 0.84 Å. For the structure of $[Zr_3(C_5H_5)_3Br_8]^+[Zr_2Br_9]^-$, the same treatment was applied for the atoms in the salt and for one ordered CH_2Cl_2 molecule in the lattice. A second CH_2Cl_2 molecule was disordered over two orientations, in a ratio of ca. 70:30. Its non-hydrogen atoms were subjected to isotropic refinement, while the hydrogen atoms were assigned idealized locations and isotropic thermal parameters and allowed to ride on their attached carbon atoms.

Results and Discussion

Synthetic Studies. The chlorination of $Zr(C_5H_5)_2Cl_2$ has served as a popular and effective route to $Zr(C_5H_5)Cl_3$, a useful starting material for further mono(cyclopentadienyl)zirconium chemistry.[2,4] However, in some cases subsequent reaction products can be contaminated with byproducts derived from formal tetrahalide species.[5,6] It is possible that these are not always present, meaning that overchlorination does not always occur, or alternatively, it is possible that overchlorination is more the rule than the exception, but the resulting products from subsequent reactions could in some cases be more soluble than those derived from $Zr(C_5H_5)Cl_3$ and, therefore might not lead to contaminants upon crystallization of the desired product. Regardless of which (or whether both) scenario may be operative, two strategies to avoid the possibility of overchlorination have been developed. In one, $Zr(C_5H_5)Cl_3(THF)_2$ is selectively crystallized from $ZrCl_4(THF)_2$,[5] while in the other, bromination of $Zr(C_5H_5)_2Cl_2$ is used to prepare $Zr(C_5H_5)Cl_2Br$ more cleanly,[6] whether due to the greater ease of controlling the amount of halogen added or to the greater selectivity of the bromination reaction, or both. The greater selectivity of bromination versus chlorination reactions with $M(C_5H_5)_2X_2$ complexes has been previously noted.[2]

Although $Zr(C_5H_5)Cl_2Br$ may be a useful reagent in situations in which all halides are to be replaced, in cases in which some halide does remain, there would be the potential for chloride/bromide disorder (*vide infra*), though in at least one example the chlorides were selectively removed by a magnesium reagent, leaving the bromide ligand coordinated to the zirconium centers.[10] One way to avoid the potential of halide disorder would be to employ $Zr(C_5H_5)Br_3$ in the desired reactions. Indeed, it had already been reported that this compound can be isolated from the bromination of $Zr(C_5H_5)_2Br_2$, though specific details were not provided.[2] Herein we report conditions under which $Zr(C_5H_5)Br_3$ may be isolated (see Experimental Section) from such a bromination process (e.g., eq 1).

$$Zr(C_5H_5)_2Br_2 + 3Br_2 \rightarrow Zr(C_5H_5)Br_3 + C_5H_5Br_5 \quad (1)$$

In order to gain some insight into the bonding of $Zr(C_5H_5)Cl_2Br$, attempts were made to bring about its crystallization. Due to the compound's insolubility in noncoordinating solvents, the attempts focused on its possible crystallization during formation. Initially these attempts were carried out at low temperatures in order to minimize the rate of reaction and, hence, crystallization. One approach was to add sufficient CH_2Cl_2 to dissolve all of the $Zr(C_5H_5)_2Cl_2$ at −78 °C, then add 3 equiv of bromine, mix briefly, and let the reaction (eq 2) slowly occur.

$$Zr(C_5H_5)_2Cl_2 + 3Br_2 \rightarrow Zr(C_5H_5)Cl_2Br + C_5H_5Br_5 \quad (2)$$

Alternatively, even when there is insufficient solvent to dissolve all of the $Zr(C_5H_5)_2Cl_2$, there is a point in the stirred

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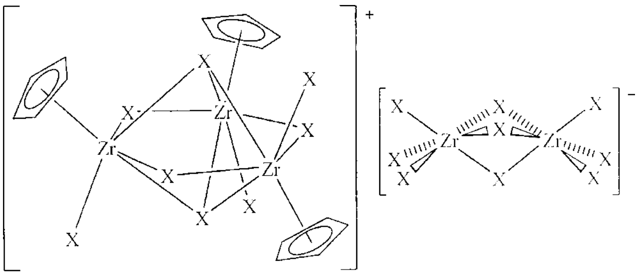
(10) Kulsomphob, V.; Arif, A. M.; Ernst, R. D. *Organometallics* **2002**, *21*, 3182.

reaction at which a clear solution is obtained, prior to crystallization of product. Cessation of mixing and continued slow warming of this mixture leads, as in the more dilute case, primarily to precipitation of microcrystalline $Zr(C_5H_5)Cl_2Br$. On standing for ca. 1–2 days, either the dilute or the more concentrated reaction mixtures would often deposit some very small pale crystals. Structural characterization revealed them to be $[Zr_3(C_5H_5)_3X_3(\mu_2\text{-}X)_3(\mu_3\text{-}X)_2]^+[Zr_2X_9]^-$ salts, **2**, with the X representing disordered composites of bromine and chlorine atoms.[11]



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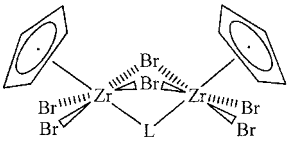
Subsequently, the bromination of $Zr(C_5H_5)_2Br_2$ was studied in order to avoid halide disorder, and it proved possible to structurally characterize two nicely ordered, related complexes, $[Zr_3(C_5H_5)_3Br_3(\mu_2\text{-}Br)_3(\mu_3\text{-}Br)(\mu_3\text{-}OH)]^+[Zr_2Br_9]^-$ and $[Zr_3(C_5H_5)_3Br_3(\mu_2\text{-}Br)_3(\mu_3\text{-}Br)_2]^+[Zr_2Br_9]^-$, the former compound being isolated as a very minor byproduct from the bromination of air-exposed $Zr(C_5H_5)_2Br_2$. The latter compound also was initially formed in very small quantities, but it proved possible to develop a route through which it could be reproducibly isolated in decent unoptimized yields from the selective overbromination of $Zr(C_5H_5)_2Br_2$ (eq 3). Eventually, well-formed crystalline samples of the originally desired $Zr(C_5H_5)Br_3$ were

$$5Zr(C_5H_5)_2Br_2 + 21\ Br_2 \rightarrow [Zr_3(C_5H_5)_3Br_3(\mu_2\text{-}Br)_3(\mu_3\text{-}Br)_2]^+[Zr_2Br_9{}^-] + 7C_5H_5Br_5 \quad (3)$$

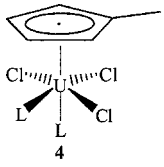
obtained by the slow, gas-phase introduction of bromine into $Zr(C_5H_5)_2Br_2$ solutions (see Experimental Section), which therefore allowed for its structure to be determined.

In some attempts to crystallize $Zr(C_5H_5)Br_3$, small amounts of crystalline, oxygen-containing products were isolated (see Experimental Section). As the $Zr(C_5H_5)_2Br_2$ starting material had been prepared from the reaction of $Zr(C_5H_5)_2Cl_2$ with an excess of BBr_3 and recrystallized, this was unexpected. Since it has been noted that $Zr(C_5H_5)_2I_2$ deteriorates on contact with air,[9] there seemed to be a possibility that $Zr(C_5H_5)_2Br_2$ could also undergo a lesser degree of deterioration. In fact, placement of $Zr(C_5H_5)_2Br_2$ in a vial with, but separated from, moist litmus paper led to the liberation of HBr, as judged by the color change in the litmus paper. Thus, coordination of water and subsequent slow hydrolysis of the $Zr(C_5H_5)_2Br_2$ on extended storage can be concluded to be the source of the oxygen-containing impurities. In one of these products, $Zr_2(C_5H_5)_2Br_4(\mu_2\text{-}Br)_2(H_2O)$, a single H_2O ligand is incorporated for two $Zr(C_5H_5)Br_3$ units, leading to a dimetallic complex that can perhaps best be described as possessing a pseudoconfacial bioctahedral arrangement, **3** ($L = H_2O$), *vide infra*.



3 ($L = H_2O$)

Structural Studies. $Zr(C_5H_5)Br_3$ has been found to be isomorphous with its chloride analogue,[8] each forming a one-dimensional chain polymer through four-membered Zr_2X_2 rings (Figure 1). The zirconium centers are each coordinated by a C_5H_5 ligand and five bromide ligands, yielding a geometry that may be best described as pseudo-octahedral. One of the equatorial bromides (Br1) is terminally bound, while the other four are involved in the bridging interactions. One of the bridging pairs involves two equatorial bromides (Br2 and Br2′), while the other pair involves the axial and one of the equatorial bromides (Br3′, Br3). As in prototypical pseudo-octahedral mono(cyclopentadienyl) complexes, such as $U(C_5H_4CH_3)Cl_3(THF)_2$[12] (**4**, L = THF) and $Er(C_5H_5)Cl_2(THF)_3$[13] (**5**, L = THF), the steric bulk of the organic ligand causes the four equatorial ligands to bend away from the organic ligand and thus out of a coplanar orientation with the metal center. In this case the Br(ax)−Zr−Br(eq) angles range from 74.05(2)° to 78.95(2)°, reflecting an average tilt of the equatorial bromine atoms by 13.2° down from their ideal pseudo-octahedral locations. The smallest Br−Zr−Br′ angle involves two bromides (Br3, Br3′) involved in a Zr_2Br_2 ring, while the other Zr_2Br_2 ring bromides (Br2, Br2′) lead to the next smallest angle, 76.63(2)°. As this pair involves two equatorial bromides, the angle between the opposite two equatorial bromides (Br1−Zr−Br3) expands to 98.04(2)°, which is significantly greater than the next largest angle, Br1−Zr−Br2 (87.96(2)°). The angular differences also appear to lead to variations in the Zr−Br distances. Likely as a result of the equatorial bromides being pushed down toward the axial bromide ligand, the Zr−Br3′ bond is the longest, at 2.8887(6) Å, while the unbridging Zr−Br1 distance is naturally shortest, at 2.5961(7) Å. That shortening presumably leads to the opposite Br2′ being second furthest from the Zr center, at 2.8213(6) Å. That leaves the intermediate Zr−Br2 (2.7584(6) Å) and Zr−Br3 (2.664(6) Å) bonds. The fact that Br3 will be opposite a C_5H_5 ligand on an adjacent zirconium coordination sphere, while Br2 will be opposite the terminal Br1 on the other adjacent zirconium center, most likely is responsible for the observed difference between these two. The average Zr−C distance is 2.510(6) Å.



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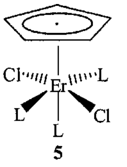

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There is a nearly constant increase in Zr−Br bond distances in $Zr(C_5H_5)Br_3$ relative to the Zr−Cl bond distances in $Zr(C_5H_5)Cl_3$. The increase for the terminal bromide is 0.177 Å, vs 0.151–0.160 Å for the bridging bromides. The increase is greater than the expected difference in either ionic or covalent

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(11) Li, C.; Ernst, R. D.; Arif, A. M. Unpublished results.

(12) Ernst, R. D.; Kennelly, W. J.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 2656.

(13) Day, C. S.; Day, V. W.; Ernst, R. D.; Vollmer, S. H. *Organometallics* **1982**, *1*, 998.

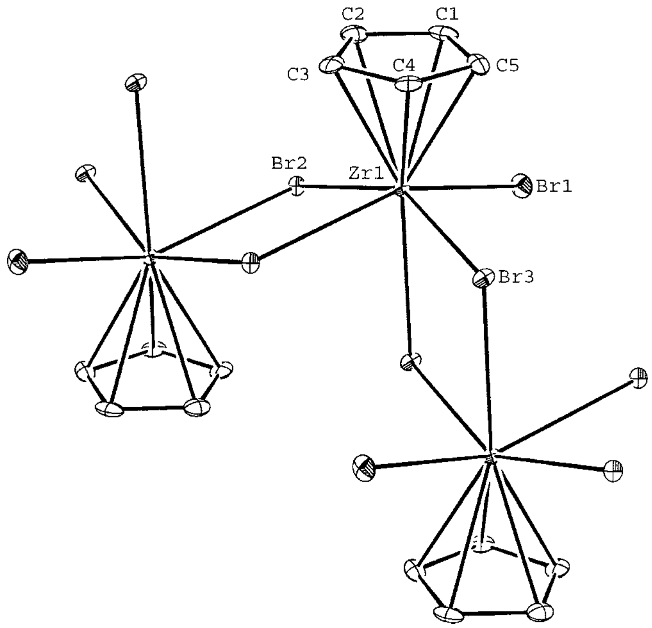

Figure 1. Perspective view of the structure of $Zr(C_5H_5)Br_3$. A center of inversion is located at the center of each Zr_2Br_2 ring. The 30% probability ellipsoids are shown.

radii, as has been observed in $M(C_5H_5)_2X_2$,[14] $M(C_5H_5)$(6,6-dmch)X_2,[15] and M(6,6-dmch)$_2X_2$[16] species.

In the dimetallic μ_2-H_2O complex, $Zr_2(C_5H_5)_2Br_4(\mu_2\text{-}Br)_2(\mu\text{-}H_2O)$, the local geometries about each Zr center involve a trans orientation of the C_5H_5 and H_2O ligands. This has been deduced to be the favored arrangement in monomeric $M(C_5H_5)L_4L'$ complexes,[12] when L′ is smaller than L, as one then has opposite the C_5H_5 ligand the smallest ligand (here, H_2O), toward which the four equatorial bromides are directed (e.g., $Zr(C_5H_5)Br_3$ structure, *vide supra*). Indeed, this arrangement has been observed for the $[Nd(C_5H_5)Cl_4(THF)]^{2-}$ coordination sphere,[17] as well as in a number of associated species including a trimetallic complex in which two zirconium centers have a similar arrangement to that in the neodymium complex, except that the oxygen coordination is provided by an oxide ion.[18] The tetrameric species $[Zr(C_5Me_5)F_2Cl]_4$[19] and $[Zr(C_5Me_5)F_2Br]_4$,[20] as well as a number of other analogues,[21] also preferentially have fluoride opposite their C_5Me_5 ligands. The closest similarity to complex **3**, however, is provided by $[Ti(C_5H_4CH_3)F_3]_2(THF)$,[22] which again has the oxygen donor center situated trans to the aromatic ligands in both coordination spheres. It is, however, relatively rare for two C_5H_5 ligands in a confacial bioctahedral $M_2(C_5H_5)_2X_7$ complex to be positioned opposite to the same atom, and perhaps the only other example is $[U_2(C_5H_5)_2Cl_7]^-$, with the remaining species having C_5H_5 ligands opposite different bridging ligands.[23,24] In contract to the above, there are actually several cases in which a small ligand resides adjacent to an aromatic cyclopentadienyl ligand.[25] Only one of these, however, is a monometallic complex, and in that case the fact that the cyclic ligand is tethered to the small ligand naturally forces a cis orientation. In other cases, the cis orientation is present in polymetallic complexes and can be attributed to the complications, steric and otherwise, that may arise in such situations.[24a,25] There are, naturally, many other complexes featuring $M(C_5H_5)X_5$ coordination spheres, in which each X represents one type of halide ligand.[26] While nearly all of these are polymetallic species, there is the interesting example of the W(VI) compound, $W(C_5Me_5)F_5$.[27] Regardless of the particular cyclopentadienyl or halide ligand present, these species all display a distortion of the four nearly coplanar basal halides toward the unique axial halide ligand.

The average Zr−O distance in $Zr_2(C_5H_5)_2Br_4(\mu_2\text{-}Br)_2(H_2O)$ is 2.450(2) Å, while the average Zr−C distance is 2.482(6) Å, a little shorter than that of the $Zr(C_5H_5)Br_3$ polymer. The Zr−Br(terminal) distances range from 2.5842(7) to 2.6118(7) Å, the shorter two being attached to Zr1, while the Zr−Br(bridging) distances range from 2.7384(7) to 2.7838(7) Å, the shorter two in this case being attached to Zr2. As a result of the Zr−Br(bridging) distances being longer than their terminal counterparts, the bridging bromides can bend down more toward the H_2O ligand before steric repulsions ensue. Thus, the O1−Zr−Br(terminal) angles average 77.8(2)°, similar to the values for the $Zr(C_5H_5)Br_3$ polymer, versus the average O1−Zr−Br(bridging) value of 70.9(4)°. As in the $Zr(C_5H_5)Br_3$ structure, the Br−Zr−Br angles for the Zr_2Br_2 rings are the smallest of the Br−Zr−Br angles (76.08(2)°, 77.08(2)°), while the Br−Zr−Br angles opposite these are the largest (96.04(2)°, 93.39(2)°). The Zr1−O1−Zr2 angle is 103.85(14)°, whereas the Zr1−Br−Zr2 angles are 88.69(2)° (Br(3)) and 88.10(2)° (Br(4)). For comparison, the Zr−Br2−Zr′ and Zr−Br3−Zr′ angles in the $Zr(C_5H_5)Br_3$ polymer are 103.37(2)° and 105.95(2)°, respectively.

The structures of the anionic and cationic portions of salt **2** (X = Br) are provided respectively in Figures 4 and 5. The arrangement of the $Zr_3(C_5H_5)_3Br_3(\mu_2\text{-}Br)_3(\mu_3\text{-}Br)_2^+$ portion of the salt is based upon a triangle of zirconium atoms, with the three μ_2-Br ligands residing nearly in this plane, and the two μ_3-Br ligands residing above and below the Zr_3 triangle. The C_5H_5 and terminal bromide ligands on each zirconium center then are located on opposite sides of the Zr_3 triangle, with two C_5H_5 ligands on one side and the remaining C_5H_5 ligand on the other (Figure 4). Zr1 therefore becomes nonequivalent to Zr2 and Zr3. This leads to local pseudo-octahedral coordination about each Zr center, similar to the coordinations observed for the $Zr(C_5H_5)Br_3$ polymer and $Zr_2(C_5H_5)_2Br_6(H_2O)$ (*vide supra*). Br7 serves as the axial bromide for Zr1, while Br8 serves as the axial bromide for both Zr2 and Zr3. Considering the μ_2-Br ligands as three-

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(14) Bush, M. A.; Sim, G. A. *J. Chem. Soc. (A)* **1971**, 2225.

(15) Rajapakshe, A.; Gruhn, N. E.; Lichtenberger, D. L.; Basta, R.; Arif, A. M.; Ernst, R. D. *J. Am. Chem. Soc.* **2004**, *126*, 14105.

(16) Basta, R.; Arif, A. M.; Ernst, R. D. *Organometallics* **2005**, *24*, 3974.

(17) Zhongsheng, J.; Ninghai, H.; Yi, L.; Xiaolong, X.; Guozhi, L. *Inorg. Chim. Acta* **1988**, *142*, 333.

(18) Hagenau, U.; Heck, J.; Kaminsky, W.; Schauwienold, A.-M. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1814.

(19) Murphy, E. F.; Lübben, T.; Herzog, A.; Roesky, H. W.; Demsar, A.; Noltemeyer, M.; Schmidt, H.-G. *Inorg. Chem.* **1996**, *35*, 23.

(20) Murphy, E. F.; Murugavel, R.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Z. Anorg. Allg. Chem.* **1996**, *622*, 579.

(21) Herzog, A.; Roesky, H. W.; Jäger, F.; Steiner, A. *Chem. Commun.* **1996**, 29.

(22) Herzog, A.; Liu, F.-Q.; Roesky, H. W.; Demsar, A.; Keller, K.; Noltemeyer, M.; Pauer, F. *Organometallics* **1994**, *13*, 1251.

(23) Arlique, T.; Ephritikhine, M.; Lance, M.; Vigner, J.; Nierlich, M. *J. Organomet. Chem.* **1994**, *484*, 195.

(24) (a) Andreu, A. M.; Jalón, F. A.; Otero, A.; Royo, P.; Lanfredi, A. M. M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1987**, 953. (b) Dias, H. V. R.; Jin, W. *J. Am. Chem. Soc.* **1996**, *118*, 9123. (c) Dias, H. V. R.; Wang, Z. *J. Am. Chem. Soc.* **1997**, *119*, 4650.

(25) Lancaster, S. J.; Thornton-Pett, M.; Dawson, D. M.; Bochmann, M. *Organometallics* **1998**, *17*, 3829.

(26) Edelman, M. A.; Hitchcock, P. B.; Hu, J.; Lappert, M. F. *New J. Chem.* **1995**, *19*, 481.

(27) Köhler, K.; Herzog, A.; Steiner, A.; Roesky, H. W. *Ang. Chem. Intl. Ed.* **1996**, *35*, 295.

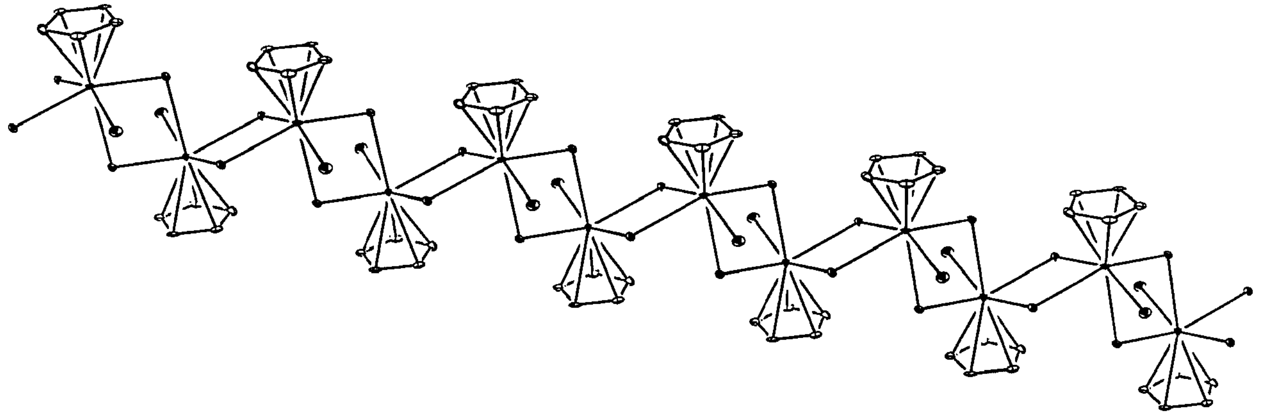

Figure 2. Extended view of the one-dimensional Zr(C_5H_5)Br$_3$ chain polymer. The 30% probability ellipsoids are shown.

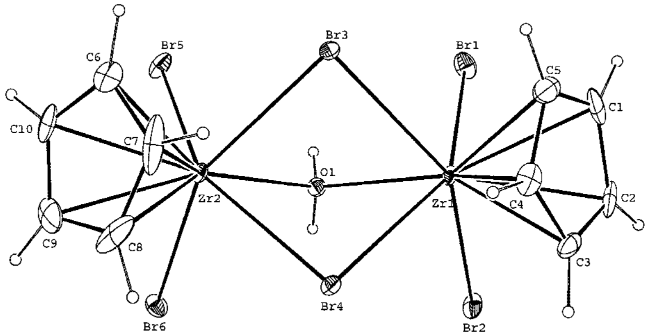

Figure 3. Perspective view of the Zr$_2$(C_5H_5)$_2$Br$_4$(μ_2-Br)$_2$(μ_2-H_2O) molecule. The 30% probability ellipsoids are shown.

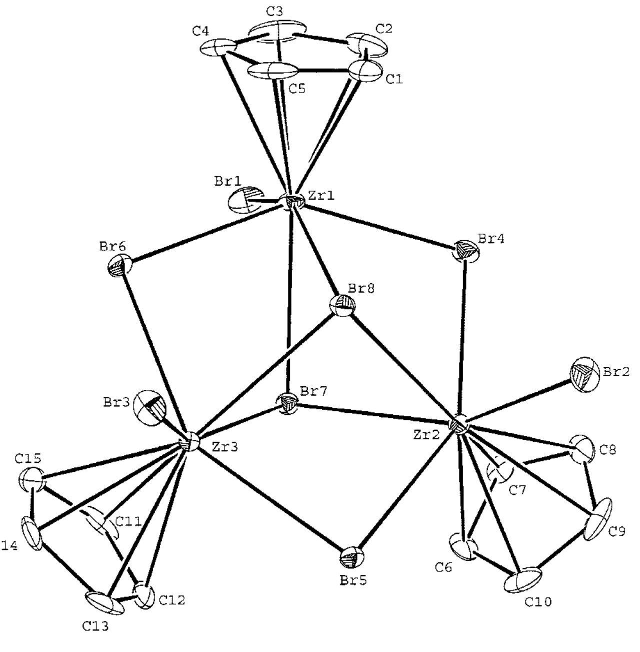

Figure 4. Perspective view of the [Zr$_3$(C_5H_5)$_3$Br$_3$(μ_2-Br)$_3$(μ_3-Br)$_2$]$^+$ ion. The 30% probability ellipsoids are shown.

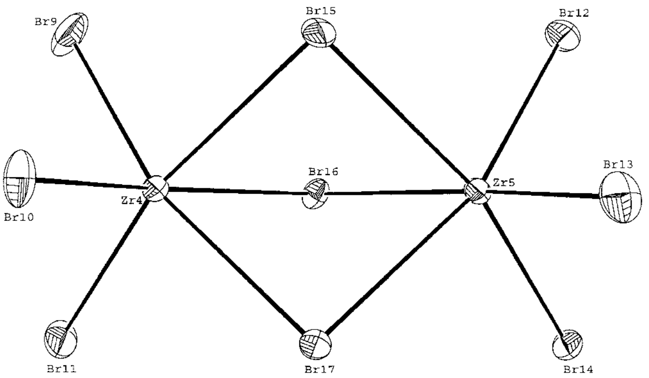

Figure 5. Perspective view of the Zr$_2$Br$_9$$^-$ ion. The 30% probability ellipsoids are shown.

electron donors and the μ_3-Br ligands as five-electron donors leads to a 16-electron count for each of the d^0 Zr(IV) centers. While there would be no metal−metal bonding for a d^0 complex, it is possible that analogous clusters with metal−metal bonds could be found for later transition metals. For tetravalent molybdenum or tungsten, there should still be no metal−metal bonding for the resulting 18-electron species (in the absence of halide rearrangements), though changes in oxidation state or use of niobium or tantalum could result in some metal−metal bonding.

For the cation, the average Zr−C distance is 2.477(4) Å, while the terminal bromide, μ_2-Br, and μ_3-Br Zr−Br distances are in the range 2.5305(13)−2.5572(13), 2.7396(14)−2.7627(14), and 2.7764(13)−2.9970(13) Å. The large variation in Zr−(μ_3-Br) distances arises from the two bonds involving the unique Zr1 center, whose bond to Br7 is the longest, and to Br8 the shortest, of those involving the two μ_3-Br ligands. The Zr−Br−Zr′ angles are all fairly close to 90°, in the range 92.59(4)−93.46(4)° for the μ_2-Br ligands and 86.73(4)−90.47(4)° for the μ_3-Br ligands. Although **2** appears to be the first example of a [M$_3$(C_5H_5)$_3$(μ_2-X)$_3$(μ_3-X)$_2$]$^+$ cluster, related arrangements have been found for [U$_3$(C_5H_5)$_6$(μ_3-Cl)$_2$(μ_2-Cl)$_3$]$^+$ and [Yb$_3$(C_5H_5)$_3$(μ_3-Cl)$_2$(μ_2-Cl)$_3$(THF)$_3$]$^+$, as well as mixed metal LiZr$_2$ and LiU$_2$ species.[23,28,29] Unlike **2**, the ytterbium complex has its three C_5H_5 ligands all on the same side of the metal triangle.

The confacial bioctahedral Zr$_2$Br$_9$$^-$ ion features average Zr−Br(terminal) and Zr−(μ_2-Br) distances of 2.500(6) and 2.774(5) Å. These values may be compared to analogous

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(28) Kretschmer, W. P.; Teuben, J. H.; Troyanov, S. I. *Angew. Chem., Int. Ed.* **1998**, *37*, 88.

(29) Butakoff, K. A.; Lemenovskii, D. A.; Mountford, P.; Kuz′mina, L. G.; Churakov, A. V. *Polyhedron* **1996**, *15*, 489.

Table 1. Crystallographic Parameters for $Zr(C_5H_5)Br_3$, $Zr_2(C_5H_5)_2Br_4(\mu_2\text{-}Br)_2(\mu_2\text{-}H_2O)$, and $[Zr_3(C_5H_5)_3Br_3(\mu_2\text{-}Br)_3(\mu_3\text{-}Br)_2]^+[Zr_2Br_9^-]$

formula	$C_5H_5Br_3Zr$	$C_{10}H_{12}Br_6OZr_2$	$C_{17}H_{19}Br_{17}Cl_4Zr_5$
fw	396.04	810.10	2179.69
temperature (K)	150(1)	150(1)	150(1)
λ (Å)	0.71073	0.71073	0.71073
cryst system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/a$
unit cell dimens			
a (Å)	6.6064(1)	10.5696(1)	17.1182(3)
b (Å)	7.1808(1)	16.7523(3)	17.3886(3)
c (Å)	9.0424(2)	11.6071(2)	17.2162(4)
α (deg)	100.6213(10)	90	90
β (deg)	92.0073(11)	116.4987(11)	111.8662(7)
γ (deg)	103.1013(13)	90	90
volume (Å^3)	409.317(12)	1839.30(5)	4755.9(2)
D_{calc}	3.213	2.925	3.044
absorp coeff (cm^{-1})	15.895	14.156	15.582
θ range (deg)	3.0 – 27.9	2.3 – 27.9	1.7 – 27.8
limiting indices	$-8 \leq h \leq 8$	$-13 \leq h \leq 13$	$-22 \leq h \leq 22$
	$-9 \leq k \leq 9$	$-20 \leq k \leq 22$	$-22 \leq k \leq 18$
	$-11 \leq l \leq 11$	$-15 \leq l \leq 15$	$-22 \leq l \leq 22$
no. of reflns collected	3512	8039	18 980
no. of indep reflns; n: $I > n\sigma(I)$	1938; 2	4379; 2	11 186; 2
$R(F)$	0.0363	0.0382	0.0586
$R_w(F^2)$	0.1116	0.0909	0.1172
max., diff Fourier peak (e Å^{-3})	1.85, −2.41	1.35, −1.64	2.14, −1.54

Table 2. Pertinent Bonding Parameters for $Zr(C_5H_5)Br_3$

Bond Distances (Å)			
Zr−C1	2.513(5)	Zr−Br1	2.5961(7)
Zr−C2	2.519(5)	Zr−Br2	2.7584(6)
Zr−C3	2.516(5)	Zr−Br3	2.6694(6)
Zr−C4	2.515(5)	Zr−Br2′	2.8213(6)
Zr−C5	2.487(5)	Zr−Br3′	2.8877(6)
Bond Angles (deg)			
Br1−Zr−Br2	87.96(2)	Br2−Zr−Br3	150.15(2)
Br1−Zr−Br3	98.04(2)	Br2−Zr−Br2′	76.63(2)
Br1−Zr−Br2′	151.94(2)	Br2−Zr−Br3′	78.95(2)
Br1−Zr−Br3′	77.04(2)	Br3−Zr−Br2′	85.06(2)
Br2−Zr−Br3′	77.07(2)	Br3−Zr−Br3′	74.05(2)

Table 3. Pertinent Bonding Parameters for $Zr_2(C_5H_5)_2Br_6(\mu_2\text{-}H_2O)$

Bond Distances (Å)			
Zr1−O1	2.453(3)	Zr2−O1	2.448(3)
Zr1−C1	2.491(5)	Zr2−C6	2.478(6)
Zr1−C2	2.469(5)	Zr2−C7	2.458(6)
Zr1−C3	2.468(5)	Zr2−C8	2.464(6)
Zr1−C4	2.481(5)	Zr2−C9	2.509(6)
Zr1−C5	2.499(6)	Zr2−C10	2.505(5)
Zr1−Br1	2.5842(7)	Zr2−Br3	2.7384(7)
Zr1−Br2	2.5892(7)	Zr2−Br4	2.7650(7)
Zr1−Br3	2.7810(6)	Zr2−Br5	2.6025(7)
Zr1−Br4	2.7838(7)	Zr2−Br6	2.6118(7)
Bond Angles (deg)			
O1−Zr1−Br1	77.73(9)	O1−Zr2−Br3	71.98(8)
O1−Zr1−Br2	77.44(9)	O1−Zr2−Br4	70.52(9)
O1−Zr1−Br3	71.15(9)	O1−Zr2−Br5	78.18(9)
O1−Zr1−Br4	70.12(9)	O1−Zr2−Br6	77.77(9)
Br1−Zr1−Br2	96.04(2)	Br3−Zr2−Br4	77.08(2)
Br1−Zr1−Br3	84.78(2)	Br3−Zr2−Br5	87.15(2)
Br1−Zr1−Br4	146.42(2)	Br3−Zr2−Br6	148.97(2)
Br2−Zr1−Br3	147.67(2)	Br4−Zr2−Br5	147.97(2)
Br2−Zr1−Br4	86.39(2)	Br4−Zr2−Br6	86.61(2)
Br3−Zr1−Br4	76.08(2)	Br5−Zr2−Br6	93.39(2)
Zr1−Br3−Zr2	88.69(2)	Zr1−Br4−Zr2	88.10(2)
Zr1−O1−Zr2	103.85(14)		

Table 4. Pertinent Bonding Parameters for $[Zr_3(C_5H_5)_3Br_3(\mu_2\text{-}Br)_3(\mu_3\text{-}Br)_2]^+[Zr_2Br_9]^-$

Bond Distances (Å)			
Zr1−C1	2.463(11)	Zr1−Br1	2.5398(14)
Zr1−C2	2.462(12)	Zr1−Br4	2.7396(14)
Zr1−C3	2.475(12)	Zr1−Br6	2.7503(14)
Zr1−C4	2.471(12)	Zr1−Br7	2.9970(13)
Zr1−C5	2.497(11)	Zr1−Br8	2.7764(13)
Zr2−C6	2.467(10)	Zr2−Br2	2.5305(13)
Zr2−C7	2.469(9)	Zr2−Br4	2.7627(14)
Zr2−C8	2.470(10)	Zr2−Br5	2.7415(13)
Zr2−C9	2.488(11)	Zr2−Br7	2.8350(13)
Zr2−C10	2.481(11)	Zr2−Br8	2.8655(13)
Zr3−C11	2.506(10)	Zr3−Br3	2.5572(13)
Zr3−C12	2.484(11)	Zr3−Br5	2.7527(13)
Zr3−C13	2.449(10)	Zr3−Br6	2.7478(14)
Zr3−C14	2.490(10)	Zr3−Br7	2.8225(13)
Zr3−C15	2.478(11)	Zr3−Br8	2.8682(13)
Zr4−Br9	2.4905(15)	Zr5−Br12	2.4887(14)
Zr4−Br10	2.5074(14)	Zr5−Br13	2.5109(15)
Zr4−Br11	2.4833(15)	Zr5−Br14	2.5200(13)
Zr4−Br15	2.7917(14)	Zr5−Br15	2.7698(14)
Zr4−Br16	2.7554(13)	Zr5−Br16	2.7663(14)
Zr4−Br17	2.7827(13)	Zr5−Br17	2.7788(13)
Bond Angles (deg)			
Zr1−Br4−Zr2	93.46(4)	Zr1−Br8−Zr2	90.47(4)
Zr2−Br5−Zr3	92.59(4)	Zr1−Br8−Zr3	90.27(4)
Zr1−Br6−Zr3	93.40(4)	Zr2−Br8−Zr3	87.69(4)
Zr1−Br7−Zr2	86.73(4)	Zr4−Br15−Zr5	85.54(4)
Zr1−Br7−Zr3	86.82(4)	Zr4−Br16−Zr5	86.31(4)
Zr2−Br7−Zr3	89.18(4)	Zr4−Br17−Zr5	85.54(4)

distances in several $Zr_2Cl_9^-$ salts,[30] whose terminal and bridging Zr−Cl distances fall in significantly broad ranges, averaging ca. 2.31–2.35 and 2.58–2.61 Å, respectively. The (μ_2-Br)−Zr−(μ_2-Br′) angles average 78.7(4)°, while the angles involving two terminal bromides average 98.2(4)°. The Zr4−Br−Zr5 angles are 85.54(4)°, 86.31(4)°, and 85.54(4)°, respectively, for Br(15–17).

Conclusions

The complex $Zr(C_5H_5)Br_3$ appears to be an ideal starting material for mono(cyclopentadienyl)zirconium chemistry, and it has been found to be isomorphous with the one-dimensional chain polymer $Zr(C_5H_5)Cl_3$. The formation of these compounds by the halogenations of zirconocene dihalides can be complicated by at least two factors. First, overhalogenation can lead to loss of both C_5H_5 ligands, although the product

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[30] (a) Chen, L.; Cotton, F. A. *Inorg. Chem.* **1996**, *35*, 7364. (b) Musso, F.; Solari, E.; Floriani, C.; Schenk, K. *Organometallics* **1997**, *16*, 4889. (c) Schormann, M.; Garratt, S.; Bochmann, M. *Organometallics* **2005**, *24*, 1718.

need not be a zirconium tetrahalide. At least one type of intermediate species can be isolated, the salt $[Zr_3(C_5H_5)_3Br_3(\mu_2\text{-}Br)_3(\mu_3\text{-}Br)_2]^+Zr_2Br_9^-$. A second complication can arise from the apparently unappreciated ability of $Zr(C_5H_5)_2Br_2$ to absorb water. Use of air-exposed $Zr(C_5H_5)_2Br_2$ in the bromination reaction can lead to additional products such as the confacial bioctahedral $Zr_2(C_5H_5)_2Br_4(\mu_2\text{-}Br)_2(\mu_2\text{-}H_2O)$ ($=[Zr(C_5H_5)Br_3]_2 \cdot H_2O$). It might well be that related complexes, in which H_2O is replaced by more elaborate bridging ligands, could be prepared directly from $Zr(C_5H_5)Br_3$ or generated during the bromination reaction, through the addition of the appropriate quantity of the bridging ligand. Presumably, the bridging ligand would not be restricted to species through which coordination to the two metal centers is provided by the same atom, so that this could provide access to a variety of interesting new species.

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Supporting Information Available: CIF files giving crystal data for the three compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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