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Preparation of the Metallocene Oxide Cluster Compound $[(Cp_2Zr)_3(\mu_2\text{-}OH)_3(\mu_3\text{-}O)^+]BPh_4^-$ by Hydrolysis of Jordan's Cation $[Cp_2ZrCH_3(THF)^+]BPh_4^-$

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Summary: The THF-stabilized methylzirconocene salt $[Cp_2ZrCH_3(THF)^+]BPh_4^-$ *(**2**) was treated with excess* H_2O *in dichloromethane/THF at −78 °C to yield the trinuclear metallocene oxide cation complex* $[(Cp_2Zr)_3(\mu_2\text{-}OH)_3(\mu_3\text{-}O)^+]BPh_4^-\cdot 3THF$ *(*$\mathbf{1}^+BPh_4^-$*) in 72% yield. The complex* $\mathbf{1}^+BPh_4^-$ *was characterized by X-ray diffraction. It exhibits a planar central* Zr_3O_3 *hexagon having the* μ_3*-O ligand in its center. Each of the three oxygen atoms at the perimeter is protonated and in the crystal connected to a THF molecule by means of a weak hydrogen bond. The byproduct* $THF\cdot BPh_3$ *(**3**) was crystallized from the THF mother liquor and identified by X-ray diffraction.*

Introduction

Cyclooligomeric group 4 metallocene oxides (and their heavier chalcogen-containing analogues) provide interesting substrates to develop homogeneous pathways of mimicking the chemistry of small reactive reagents (e.g., of the methylene group or even of a proton) on metal oxide surfaces. We have demonstrated this, for instance, by observing Fischer−Tropsch-type behavior of CH_2 groups edge-on-bonded to the framework of the $(Cp_2ZrO)_3$ pseudohexagonal framework.[1] In contrast to the related $Cp_2Zr{=}NR$ species, which are readily formed by β-elimination pathways,[2] the group 4 metallocene oxides are often prepared by oxidative pathways, such as treatment of the respective Cp_2M^{II} substrates with a very mild oxidizing reagent, such as N_2O[3] or even CO_2.[4] Hydrolytic formation of group 4 metallocene oxide frameworks is less common, mostly because such reactions tend to be ill-defined and are, therefore, of less practical use than the established oxidative routes. However, it is of considerable importance to develop reliable hydrolytic syntheses in group 4 metallocene chemistry, since a variety of interesting frameworks can apparently only be prepared in this way.[5]

An interesting example is the $[(Cp_2Zr)_3(\mu_2\text{-}OH)_3(\mu_3\text{-}O)^+]$ cation ($\mathbf{1}^+$), which had been obtained a while ago by Majoral et al. in small yield as an unexpected hydrolysis product during treatment of a phosphorus-substituted (η^2-iminoacyl)zirconocene complex.[6] The X-ray crystal structure analysis of the triflate $\mathbf{1}^+OTf^-$ had problems concerning the hydrogen positions at the μ_2-bridging oxygen atoms. We have now developed a reliable hydrolytic pathway that makes the analogous salt $[(Cp_2Zr)_3(\mu_2\text{-}OH)_3(\mu_3\text{-}O)^+]BPh_4^-$ ($\mathbf{1}^+BPh_4^-$) available in good yield (>70%) after recrystallization from tetrahydrofuran, and we have characterized it as a THF solvate by a good X-ray crystal structure analysis, which is reported in this Note.

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† X-ray crystal structure analyses.

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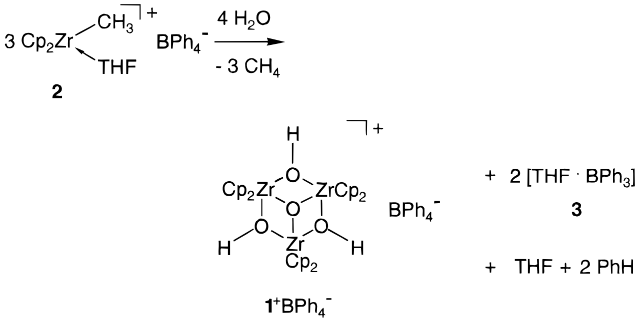
Scheme 1. Formation of $1^{+}BPh_4^{-}$ by Hydrolysis of 2



Results and Discussion

The hydrolysis reaction of $[Cp_2ZrCH_3(THF)^+]BPh_4^-$ [7] (**2**) was carried out in a dichloromethane/tetrahydrofuran (ca. 10:1) solution. In a preliminary experiment a "titration" of **2** with increasing amounts of H_2O was carried out in THF-d_8 with direct ^{1}H NMR control to determine the necessary amount of water to be added to achieve a complete and defined product formation. Under these conditions the Cp signal of an as yet unidentified reactive intermediate (δ 6.29 ppm) was observed, followed by the appearance of a secondary product ($\mathbf{1}^+BPh_4^-$, δ 6.24 (Cp)) which was stable under the applied hydrolysis conditions and could eventually be obtained on a preparative scale and isolated.

$\mathbf{1}^+BPh_4^-$ was synthesized on a preparative scale by treatment of the "Jordan cation" (**2**) with ca. 5 molar equiv of water in dichloromethane/tetrahydrofuran at −78 °C and isolated in ca. 70% yield. It is characterized by the occurrence of ^{1}H NMR signals at δ 6.34 (Cp) and δ 2.84 (μ_2-OH) in a 10:1 intensity ratio (^{13}C NMR: δ 114.2 ppm), in addition to the BPh_4^- anion NMR resonances, and a pronounced OH band in the IR spectrum at $\tilde{\nu}$ 3567 cm^{-1} (in KBr). The mass spectrum showed a parent peak corresponding to the trinuclear cation $[(Cp_2Zr)_3(\mu_2\text{-}OH)_3(\mu_3\text{-}O)^+]$ (*m/z* 731) with its characteristic isotope pattern.

Single crystals of $\mathbf{1}^+BPh_4^-$ were obtained by recrystallization from tetrahydrofuran. The crystalline material that was isolated contained five molecules of the THF solvent in the unit cell. Three of these are in contact with the cation $\mathbf{1}^+$ (see below); the other two were found (disordered) at more remote positions in the lattice. Cations and anions of $\mathbf{1}^+BPh_4^-$ are well-separated in the crystal.

The cation of $\mathbf{1}^+BPh_4^-$ contains three Cp_2Zr bent metallocene units that are connected by three μ_2-OH groups and a single μ_3-O ligand in a distorted-hexagonal array. The cation is close to C_{3v} symmetric, but not strictly crystallographically so. The central $[Zr_3(\mu_2\text{-}OH)_3(\mu_3\text{-}O)]$ framework of $\mathbf{1}^+BPh_4^-$ is practically planar. The O−Zr−O angles at the periphery are all close to 130° (for detailed values see Figure 1), and the Zr−O−Zr angles at the peripheral oxygen atoms are between 107 and 109°. The sum of the six peripheral angles amount to 719.9°, which is practically identical with the expected 720° value of a planar C_{3v}-distorted regular hexagon. The central μ_3-O ligand is planar-tricoordinated to the three zirconium atoms. The sum of the bond angles at the central oxygen atom (O4) amounts to 359.1°. As expected, the three diamond-shaped substructures of the hexagonal central framework have sums of bonding angles very close to 360° (359.9, 359.8, and 359.8°; for the individual bond angles see Figure 1).

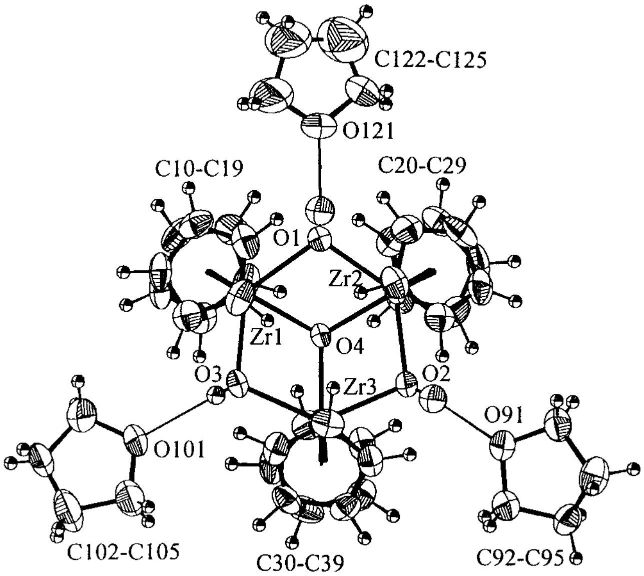


Figure 1. Molecular structure of the cation $\mathbf{1}^+$. Selected bond lengths (Å) and angles (deg): Zr1−O1 = 2.188(2), Zr1−O3 = 2.187(3), Zr1−O4 = 2.070(2), Zr2−O1 = 2.190(3), Zr2−O2 = 2.215(2), Zr2−O4 = 2.060(2), Zr3−O2 = 2.212(2), Zr3−O3 = 2.186(3), Zr3−O4 = 2.052(2), averaged Zr−(μ_2-O) = 2.196, Zr−(μ_3-O) = 2.061, O1···O121 = 2.699(6), O2···O91 = 2.949(7), O3···O101 = 2.788(7); O1−Zr1−O3 = 130.9(1), O1−Zr1−O4 = 65.7(1), O3−Zr1−O4 = 65.4(1), O1−Zr2−O2 = 131.8(1), O1−Zr2−O4 = 65.8(1), O2−Zr2−O4 = 66.2(1), O2−Zr3−O3 = 131.9(1), O2−Zr3−O4 = 66.4(1), O3−Zr3−O4 = 65.7(1), Zr1−O1−Zr2 = 109.0(1), Zr2−O2−Zr3 = 107.2(1), Zr1−O3−Zr3 = 109.1(1), Zr1−O4−Zr2 = 119.3(1), Zr1−O4−Zr3 = 119.6(1), Zr2−O4−Zr3 = 120.1(1), averaged Zr−(μ_2-O)−Zr = 108.4, (μ_2-O)−Zr−(μ_2-O) = 131.5, Zr−(μ_3-O)−Zr = 119.7.

The Zr−(μ_3-O) bond lengths to the central oxygen atom are within a close range (Zr1−O4 = 2.070(2) Å, Zr2−O4 = 2.060(2) Å, Zr3−O4 = 2.052(2) Å). The Zr−(μ_3-O) bonds are shorter than the peripheral Zr−(μ_2-OH) bonds, which were found in a range between 2.186(3) Å (Zr3−O3) and 2.215(2) Å (Zr2−O2). The oxygen atoms at the hexagonal perimeter of $\mathbf{1}^+BPh_4^-$ each bear a hydrogen atom bonded to them, which was located in the structure solution. Three tetrahydrofuran molecules are located close to C_3 symmetric around the $[(Cp_2Zr)_3(\mu_2\text{-}OH)_3(\mu_3\text{-}O)^+]$ core of the molecule, with their oxygen atoms connected by weak hydrogen bonds to the organometallic trinuclear metallocene oxide framework (the respective THF(oxygen)···metallocene oxide (oxygen) distances amount to O1···O121 = 2.699(6) Å, O3···O101 = 2.788(7) Å, and O2···O91 = 2.949(7) Å).[8]

The observed hydrolysis reaction requires a mechanistic scheme which takes into account that three metallocene units, each originating from a mononuclear

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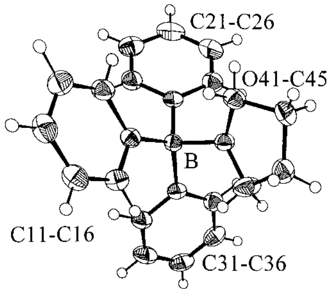

Figure 2. Molecular structure of THF·BPh_3 (**3**), the byproduct obtained in the hydrolysis reaction of $[Cp_2ZrCH_3(THF)^+]BPh_4^-$.

monocation, eventually get combined to a trimetallic organometallic monocation. This means that the fate of the two remaining BPh_4^- counteranions must be accounted for. These would appear in the formal equation as $[H_3O^+BPh_4^-]$, but this strong acid is probably not stable under the applied conditions and seems to eventually give rise to the formation of BPh_3 and benzene. A tentative reaction sequence is provided with the Supporting Information.[9] There is some indication that the formation of triphenylborane indeed makes a significant contribution to the overall reaction scheme: from the THF mother liquor of the synthesis of $\mathbf{1}^+BPh_4^-$ on a preparative scale single crystals of the adduct THF·BPh_3 (**3**) were obtained and identified by X-ray diffraction (see Figure 2).[10]

Experimental Section

Hydrolysis Reaction of $[Cp_2ZrCH_3(THF)^+]BPh_4^-$ (2): Formation of $[(Cp_2Zr)_3(\mu_2\text{-}OH)_3(\mu_3\text{-}O)^+]BPh_4^-$ ($\mathbf{1}^+BPh_4^-$). The starting material $[Cp_2ZrCH_3(THF)^+]BPh_4^-$ (**2**) was synthesized by treatment of dimethylzirconocene with tri-*n*-butylammonium tetraphenylborate in THF. Complex **2** (2.80 g, 4.48 mmol) was dissolved in 100 mL of dichloromethane. The solution was cooled to −78 °C. Then 3.56 mL of a 6.39 M solution of H_2O (22.7 mmol) in THF was added. The mixture was stirred for 2 h at −78 °C, and then cold pentane was added to precipitate the product. After 15 min at −78 °C the solid product was collected by filtration. The product was recrystallized from tetrahydrofuran and dried in vacuo to yield 1.13 g (72%) of close to analytically pure $\mathbf{1}^+BPh_4^-$, mp 65 °C dec. Anal. Calcd for $C_{54}H_{53}O_4BZr_3$ (1050.5): C, 61.74; H, 5.09. Found: C, 61.99; H, 5.69. MS (ESI, 39 V): *m*/*z* 731 (M^+), 713 ($M^+ - H_2O$). IR (KBr): $\tilde{\nu}$ 3567 (s, OH), 3057, 1481, 1027, 813 cm^{-1}. ^1H NMR (200 MHz, THF-d_8): δ 6.34 (s, 30H, Cp), 2.84 (s, 3H, μ_2-OH); $[BPh_4^-]$ δ 7.35 (m, 8H, *o*-Ph), 6.87 (m, 8H, *m*-Ph), 6.75 (m, 4H, *p*-Ph). ^{13}C NMR (50 MHz, THF-d_8): δ 114.2 (Cp); $[BPh_4^-]$, δ 137.4, 125.7, 121.8 (*o*-, *m*-, *p*-Ph; ipso-C of Ph not found). ^{11}B NMR (64 MHz, THF-d_8): δ −6.5 (BPh_4^-).

X-ray Crystal Structure Analyses. $\mathbf{1}^+BPh_4^-$. Single crystals were obtained by recrystallization from tetrahydrofuran. Crystal data: formula $C_{74}H_{93}O_9BZr_3$, $M_r = 1410.95$, light yellow crystal, 0.20 × 0.10 × 0.05 mm, $a = 12.861(1)$ Å, $b = 13.985(1)$ Å, $c = 18.903(1)$ Å, $\alpha = 101.68(1)°$, $\beta = 90.15(1)°$, $\gamma = 92.41(1)°$, $V = 3326.4(4)$ Å^3, $\rho_{calcd} = 1.409$ g cm^{-3}, $\mu = 5.18$ cm^{-1}, empirical absorption correction via SORTAV ($0.904 \leq T \leq 0.975$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.710\,73$ Å, $T = 198$ K, ω and φ scans, 52 789 reflections collected ($\pm h, \pm k, \pm l$), $(\sin\theta)/\lambda = 0.65$ Å^{-1}, 15 251 independent ($R_{int} = 0.052$) and 11 656 observed reflections ($I \geq 2\sigma(I)$), 796 refined parameters, R1 = 0.047, wR2 = 0.100, maximum residual electron density 0.76 (−0.81) e Å^{-3}, hydrogens at bridging oxygens from difference Fourier map, others calculated and all refined riding, thermal parameters of the THF molecules indicate some positional nonrefined disorder.

3. From the THF mother liquor, which remained from the recrystallization of $\mathbf{1}^+BPh_4^-$, single crystals of the THF·BPh_3 adduct **3** were obtained. Compound **3** was identified by an X-ray crystal structure analysis. Crystal data: formula $C_{22}H_{23}OB$, $M_r = 314.21$, colorless crystal 0.40 × 0.20 × 0.05 mm, $a = 9.109(1)$ Å, $b = 12.767(3)$ Å, $c = 15.628(5)$ Å, $\beta = 104.66(2)°$, $V = 1758.3(7)$ Å^3, $\rho_{calcd} = 1.187$ g cm^{-3}, $\mu = 5.32$ cm^{-1}, empirical absorption correction via ψ scan data ($0.815 \leq T \leq 0.974$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 1.541\,78$ Å, $T = 223$ K, $\omega/2\theta$ scans, 3715 reflections collected ($\pm h, -k, +l$), $(\sin\theta)/\lambda = 0.62$ Å^{-1}, 3581 independent ($R_{int} = 0.030$) and 2849 observed reflections ($I \geq 2\sigma(I)$), 217 refined parameters, R1 = 0.044, wR2 = 0.123, maximum residual electron density 0.24 (−0.29) e Å^{-3}, hydrogens calculated and riding.

Data sets were collected with Enraf-Nonius CAD4 or Nonius KappaCCD diffractometers, the latter being equipped with a Nonius FR591 rotating anode generator. Programs used: data collection EXPRESS (Nonius BV, 1994) or COLLECT (Nonius BV, 1998); data reduction MolEN (K. Fair, Enraf-Nonius BV, 1990) or Denzo-SMN;[11] absorption correction for CCD data SORTAV;[12] structure solution SHELXS-86 or SHELXS-97;[13] structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, 1997); graphics (with unsystematical numbering schemes) DIAMOND (K. Brandenburg, Universität Bonn, 1996) and SCHAKAL (E. Keller, Universität Freiburg, 1997).

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Supporting Information Available: IR and MS spectra of $\mathbf{1}^+$, tables giving details of the X-ray crystal structure analyses of complexes $\mathbf{1}^+BPh_4^-$ and **3**, and a figure giving the tentative reaction sequence. This material is available free of charge via the Internet at http://pubs.acs.org.

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