Inorg. Chem. **1998,** *37,* 3471−3474 **3471**

Variation in the Mode of Coordination of Aryl Sulfonates to Zirconocene in the Solid State

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Received December 26, 1997

The solid-state structures of three zirconocene aryl sulfonates were determined. In $Cp_2Zr(OSO_2C_6H_5)_2$ (**1**), one of the sulfonate ligands is monodentate, the other bidentate coordinated. $Cp_2Zr(OSO_2\text{-}4\text{-}C_6H_4Cl)_2$ (**2**) and $Cp_2Zr(OSO_2\text{-}3,4\text{-}C_6H_3Cl_2)_2$ (**3**) are dimers of pentacoordinated zirconocenes with two monodentate sulfonates and a double bridge of μ-O,μ-O′-sulfonates. A possible explanation for the formation of the solid-state structures is offered in terms of differences in electron density of the sulfonate oxygen atoms. **1**: $C_{22}H_{20}O_6S_2Zr$, a = 8.062(2) Å, b = 14.502(3) Å, c = 19.623(4) Å, α = 90.91(1)°, β = 101.78(1)°, γ = 106.00(2)°, triclinic, $P\bar{1}$, Z = 4. **2**: $C_{22}H_{18}Cl_2O_6S_2Zr$, a = 7.9669(8) Å, b = 11.0816(12) Å, c = 13.4056(10) Å, α = 79.944(7)°, β = 75.009(7)°, γ = 84.647(9)°, triclinic, $P\bar{1}$, Z = 2. **3**: $C_{22}H_{16}Cl_4O_6S_2Zr$, a = 7.7574(7) Å, b = 12.1124(12) Å, c = 13.4613(11) Å, α = 85.343(7)°, β = 76.653(6)°, γ = 79.880(8)°, triclinic, $P\bar{1}$, Z = 2.

Introduction

Recently we started an investigation on the reactivity of zirconocene derivatives with coordinating sulfonates.[1] It was found that the effective charge on zirconium depends linearly on that of the sulfonate group and, thus, is a powerful tool to adjust the Lewis acidity of the central metal. We could for example show that the ^{11}B NMR shift of zirconocene tetrahydroborate aryl sulfonate complexes $Cp_2ZrBH_4(OSO_2R)$ correlates with the Hammett parameters of the substituents of the aryl group.[2] This is also reflected in the chemistry of the hydrozirconation reagents of the type $Cp_2ZrH(OSO_2R)$ with R = aryl.[3] We have discovered that the solid-state structure of zirconocene bis(aryl sulfonates), key intermediates into this chemistry, is also very much affected by the type of sulfonate. An X-ray structure determination of three derivatives of $Cp_2Zr(OSO_2R)_2$, with R = phenyl (**1**), R = 4-chlorophenyl (**2**), and R =3,4-dichlorophenyl (**3**) was carried out. The outcome shows a remarkable variation in coordination geometry, none of which equals that of the known structure of the tosyl derivative $Cp_2Zr(OSO_2\text{-}4\text{-}C_6H_4Me)_2$ (**4**) which was reported by Thewalt[4] about 10 years ago. There, a tetracoordinated zirconocene with two monodentate sulfonates was obtained, the preferential coordination of both $Cp_2Zr(IV)$ and sulfonates to transition metals.[5]

Results

It was much to our surprise that, in the solid-state structure of the phenyl sulfonate derivative $Cp_2Zr(OSO_2Ph)_2$ (**1**), a pentacoordinated zirconocene was found (Figure 1) with one monodentate and one bidentate coordinating RSO_3^- group. Compound **1** crystallizes in the $P\bar{1}$ space group with four molecules in the unit cell: two pairs that are slightly different (Figure 1). The three oxygen atoms coordinating to Zr lie in a plane (mean deviation: 0.0276 Å) that is about orthogonal to the plane of CE1, CE2, and Zr: the dihedral angles CE1,2−Zr−O2−O3,6 have a mean of 89.9° (ranging from 82.3° to 94.3°). Other distances and angles are as might be expected.[5]

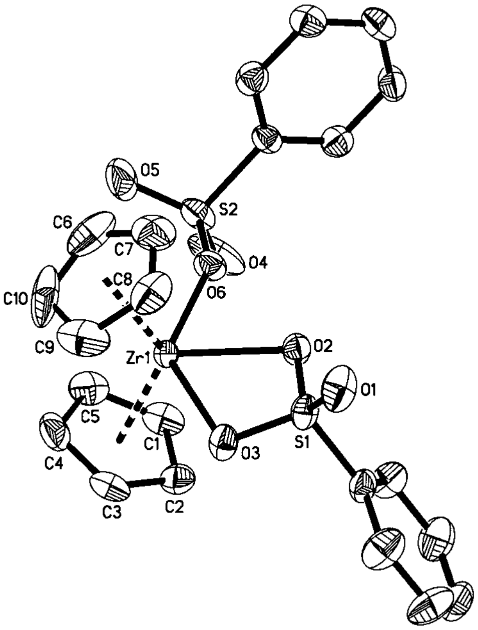

Figure 1. Solid-state structure of $Cp_2Zr(OSO_2Ph)$ (**1**) (ellipsoids drawn at 50% probability level, H atoms omitted). Selected distances (Å) and angles (deg): CE1−Zr 2.214, CE2−Zr 2.209, Zr−O6 2.135(3), Zr−O2 2.264(3), Zr−O3 2.326(2); CE1−Zr−CE2 130.1, O6−Zr−O2 73.4(1), O2−Zr−O3 60.7(1), O3−Zr−O6 134.0(1), Zr−O2−S1−O1 121.3 (one of two slightly different molecules is shown). CE1: [C(1)···C(5)] ring centroid. CE2: [C(6)···C(10)] ring centroid.

Bidentate coordination of a sulfonate to *one* metal center is quite unusual; the only other example in the Cambridge Database was that of a silver triflate (OTf) complex.[6] Very recently, however, Floriani[7] found the same coordination in the

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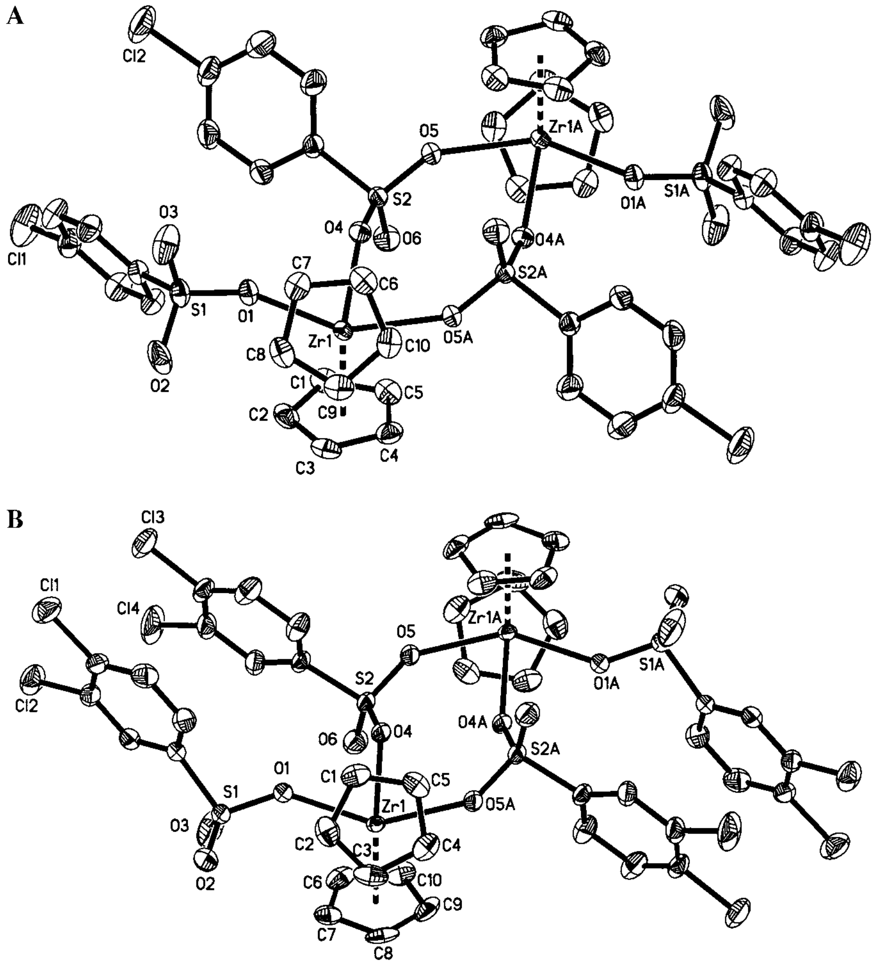

Figure 2. (A) Solid-state structure of $Cp_2Zr(OSO_2Ph\text{-}4\text{-}Cl)$ (**2**) (ellipsoids drawn at 50% probability level, H atoms omitted). Selected distances (Å) and angles (deg): CE1−Zr 2.222, CE2−Zr 2.212, Zr−O1 2.2191(15), Zr−O4 2.1958(14), Zr−O5A 2.3025(14); CE1−Zr−CE2 128.7, O1−Zr−O4 73.71(6), O4−Zr−O5A 72.81(5), O1−Zr−O5A 145.26(5). CE1: [C(1)···C(5)] ring centroid. CE2: [C(6)···C(10)] ring centroid. (B) Solid-state structure of $Cp_2Zr(OSO_2Ph\text{-}3,4\text{-}Cl_2)$ (**3**) (ellipsoids drawn at 50% probability level, H atoms omitted). Selected distances (Å) and angles (deg): CE1−Zr 2.213, CE2−Zr 2.202, Zr−O1 2.204(2), Zr−O4 2.208(2), Zr−O5A 2.294(2); CE1−Zr−CE2 128.4, O1−Zr−O4 73.33(6), O4−Zr−O5A 71.50(6), O1−Zr−O5A 144.71(6). CE1: [C(1)···C(5)], CE2: [C(6)···C(10)] ring centroid.

compounds (p-^{t}Bu-calix[4]-(O)$_2$(OMe)$_2$Zr(OTf)$_2$ and (p-^{t}Bu-calix[4]-(O)$_3$(OMe)Zr(OTf)C_5H_5N, and van Koten[8] in [Ti(η^3-*mer*-NCN)(O-*i*-Pr)(OTf)$_2$]. It may be anticipated that the metal atom in the latter complexes has an enhanced Lewis acidity compared to that in metallocene derivatives. A higher Lewis acidity increases the tendency to pentacoordination in zirconocenes.[9]

To investigate whether electronic factors are indeed important for the coordination mode of the sulfonate, we set out to crystallize $Cp_2Zr(OSO_2\text{-}4\text{-}C_6H_4Cl)_2$ (**2**). *p*-Chlorophenyl sulfonate is sterically like *p*-toluene sulfonate but is even more electron deficient than phenyl sulfonate.[10] X-ray suitable crystals were obtained by diffusing pentane into a THF solution of **2**. The molecular structure could be determined (Figure 2A), but instead of getting a structure type as in **1** or **4**, yet another coordination geometry was found. Analogously to **1**, a pentacoordinated zirconocene with bidentate sulfonates was formed, but **2** is a dimer of zirconocenes with two μ,η^2-O-bidentate bridging and two terminal sulfonates. Such bridging sulfonates are also rarely observed in complexes where the intermetallic distance is not fixed by other ligands:[11] it deserves mentioning that a similar geometry was found in a scandium compound with the electron-poor *p*-nitro sulfonate.[11a] The eight-membered ring of two Zr, two S, and four O atoms in **2** is in a chair-type conformation. The coordinating oxygen atoms and zirconium are, as in **1**, almost in a plane (mean deviation: 0.0817 Å) that

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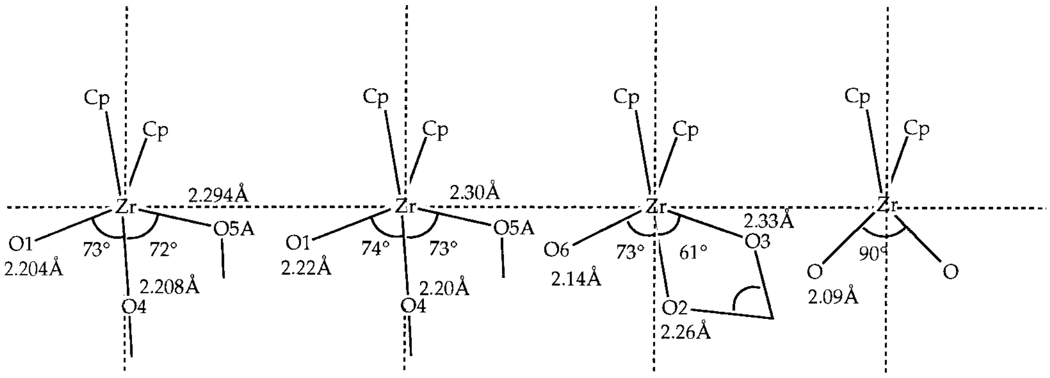

$Cp_2Zr(OSO_2\text{-}3,4\text{-}Ph\text{-}Cl_2)_2$ (**3**) $Cp_2Zr(OSO_2\text{-}4\text{-}Ph\text{-}Cl)_2$ (**2**) $Cp_2Zr(OSO_2Ph)_2$ (**1**) $Cp_2Zr(OSO_2\text{-}4\text{-}Ph\text{-}Me)_2$ (**4**)

Figure 3. Coordination geometry of Zr in **1**−**4** in the equatorial plane.

Table 1. Crystal Data

compd/formula/fw	**1**/$C_{22}H_{20}O_6S_2Zr$/535.7	**2**/$C_{22}H_{18}Cl_2O_6S_2Zr$/604.6	**3**/$C_{22}H_{16}Cl_4O_6S_2Zr$/673.49
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
lattice constants			
a	8.062(2) Å	7.9669(8) Å	7.7574(7) Å
b	14.502(3) Å	11.0816(12) Å	12.1124(12) Å
c	19.623(4) Å	13.4056(10) Å	13.4613(11) Å
α	90.91(1)°	79.944(7)°	85.343(7)°
β	101.78(1)°	75.009(7)°	76.653(6)°
γ	106.00(2)°	84.647(9)°	79.880(8)°
volume	2150.0(8) $Å^3$	1124.2(2) $Å^3$	1210.4(2) $Å^3$
Z	4	2	2
ρ(calc)	1.655 g/cm^3	1.786 g/cm^3	1.848 g/cm^3
radiation	Mo Kα ($\lambda = 71.073$ pm)	Mo Kα ($\lambda = 71.073$ pm)	Mo Kα ($\lambda = 71.073$ pm)
temp (K)	223	228	238
abs coeff	0.724 mm^{-1}	0.952 mm^{-1}	1.108 mm^{-1}
final R indices (obs data)[a]	$R(F) = 0.0364$, $R_w(F) = 0.0486$	$R(F) = 0.0271$, $R_w(F^2) = 0.0694$	$R(F) = 0.0276$, $R_w(F^2) = 0.0662$

[a] R indices based on F are denoted $R(F)$, and those on F^2, $R_w(F^2)$, e.g., $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w(F^2) = \{[\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

again is approximately the equatorial plane (dihedral angles CE1,2−Zr−O4−O1,5A have a mean of 90°: between 83.3 and 96.8°).

The solid-state structure of $Cp_2Zr(OSO_2\text{-}3,4\text{-}C_6H_3Cl_2)_2$ (**3**) was also obtained. Compound **3** crystallizes in the same space group as **1** and **2** ($P\bar{1}$ with two molecules in the unit cell). Distances and angles around Zr are very similar to those in **2** (Figures 2B and 3). The dissimilarities seem to be caused by packing effects. In both **2** and **3**, a close intermolecular contact is present between the para chloride of the phenyl ring of the bridging sulfonate (mean d(Cl−C) = 4.085 Å) and that of the same phenyl ring of the next unit and vice versa. The main difference between both structures is the orientation of the phenyl group of the bridging relative to that of the terminal sulfonate. In **2** an angle of 50.4° is found, but in **3**, the aryl groups are almost coplanar (7.2°) with an intramolecular alignment of the meta and para chlorides ($d(\mathrm{Cl1{-}Cl3})_{para}$ = 3.4 Å, $d(\mathrm{Cl2{-}Cl4})_{meta}$ = 3.6 Å). Relative to **2**, the phenyl group in **3** of the bridging sulfonates is rotated about 50° around the S−C bond (the dihedral angle O4−S2−C17−C18 is 48.1° in **2**, 96.9° in **3**) along with smaller differences in the eight-membered ring (the dihedral angle Zr−O4−S2−O6 is 1° in **2**, 15.4° in **3**). In this orientation, in addition to the intermolecular contacts between the phenyl group and chloride atom of the bridging sulfonates (mean d(Cl−C) = 3.621 Å), similar ones are present between those of the terminal sulfonates (at the same distance). This gives an alternating alignment of Cl and Ph groups throughout the crystal. The resulting intermolecular attractive interaction thus yields a more compact structure (d(Zr1−Zr1a) = 5.99 Å in **2**, 5.89 Å in **3**) with a more strongly puckered eight-membered ring.

Discussion

X-ray studies of transition metal compounds with coordinating sulfonates have mainly been performed on triflate or fluorosulfate complexes: the predominantly observed coordination mode is monodentate.[5a,b] It is therefore remarkable that four structurally characterized zirconocene sulfonates show three different types of coordination geometry which are not commonly observed. No features that could explain the difference between the solid-state structures of the $Cp_2Zr(OSO_2C_6H_{5-x}X_x)_2$ (**1**−**4**) are obvious. Apart from the ones mentioned, packing effects were not apparent in structures **1**−**4**. We propose that a different Lewis acidity of the Cp_2Zr entity in **1**−**4** underlies the difference in solid-state structure. Of course, the electronic differences between the various substituted phenyl sulfonic acids are not large, but may be a decisive factor in the formation of the solid-state structure. In $CDCl_3$ solution, the compounds seem to be monomeric with equivalent sulfonate groups.[2]

From the viewpoint of the common part of **1**, **2** (≈**3**), and **4**, the strong Lewis acidic zirconocene dication Cp_2Zr^{2+}, an explanation from electronic arguments for the sulfonate coordination mode may be given. Monodentate coordination of one sulfonate gives $Cp_2Zr\text{-}\eta^1\text{-}OSO_2C_6H_{5-x}X_x^+$, a cation with a reduced Lewis acidity that will be dependent on the type of sulfonate.[1−3] In the case of the most electron rich sulfonate (in compound **4**) the Lewis acidity of Zr in $Cp_2Zr\text{-}\eta^1\text{-}OSO_2C_6H_4\text{-}Me^+$ is diminished to such an extent that no driving force is left for the coordination of a third oxygen atom after monodentate binding of the second tosyl anion. This is different for the imaginary $Cp_2Zr\text{-}\eta^1\text{-}OSO_2C_6H_5^+$ cation: the oxygen atoms of phenyl sulfonate have a lower electron density, and the remaining electron deficiency of the cationic Cp_2Zr-η^1-$OSO_2C_6H_5^+$ induces a bidentate coordination of the second $^-OSO_2C_6H_5$ anion. The same is the case for **2**, but here an additional stabilization is apparently gained through the formation of dimers. From a statistical analysis of nonconstrained $Cp_2Zr(OX)_3$ it can be recognized that the most favorable angle between the lateral oxygen atom, zirconium, and the central oxygen atom is ≈72°. This is, as shown in Figure 3, not attainable through a η^2-sulfonate coordination as in **1**, but through bridging. Hence as soon as enough binding enthalpy is attained in the more favorable geometry, the negative entropy for aggregate formation can be overcome, and structures such as **2** form.

It is interesting to compare angles and distances around zirconium in **1**, **2** (≈ **3**), and **4** (Figure 3). The Zr−O bond length of the terminal sulfonate increases from **4** to **1** to **2**. It indicates that, in the pentacoordinated zirconocenes **1** and **2**, the electron density on Zr is higher than in **4**, and in **2** even higher than in **1**. In the sterically nonconstrained geometry of **2**, electron donation from the lateral oxygen atom of the bridging sulfonate is more effective than in **1** where both coordinating oxygen atoms are in a position that is a compromise: the central oxygen atom is moved from the optimum position along the C_2 axis and the terminal one cannot reach the same position as in **2** (the angle O3−Zr1−O2 is restrained by the O3−S1−O2 angle of 102.9°).[12] The central Zr−O bond length decreases from **1** to **2** as expected.

The description given for the coordination geometry of $Cp_2Zr(OSO_2R)_2$ affords a consistent view. However, as may be concluded from the ^1H NMR properties,[2] the effects Lewis acidity has on the sulfonate coordination mode are small and other factors may be adversely responsible for the differences in structure.

Experimental Section

Compounds were prepared, characterized and handled by procedures previously described.[2] X-ray suitable crystals (colorless) were obtained by diffusing pentane into a concentrated THF solution of compounds **1**−**3**. For further details see Table 1.

Acknowledgment. G.A.L. thanks the Alexander von Humboldt Foundation for a Fellowship. N.S.H., F.S., and K.S. acknowledge the support from “Land Baden-Württemberg” in form of a “Landesgraduierten Stipendium”.

Supporting Information Available: Tables containing distances and angles in **1**−**4** and a statistical analysis of pentacoordinated zirconocenes and a discussion of the unit cell and intermolecular interactions in **1**−**3** including figures (10 pages). Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles for compounds **2** and **3** are available, in a CIF format file, on the Internet only. Ordering and Internet access information is given on any current masthead page.

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(12) This is also obvious from the distances of O2, O3, and O6 to the CE1−CE2−Zr plane in **1** of −0.36, −2.18, and 1.91 Å; the corresponding distances (O1, O4, O5a) are −2.069, 0.1617, and 2.2382 Å in **2** and 1.478 Å in **4**.