Organometallic Supramolecular Chemistry with Monosaccharides: Triethylammonium μ-Chloro-bis{chloro(η^5-cyclopentadienyl)-(methyl 4,6-*O*-benzylidene-β-D-glucopyranosidato-1κO^2,1:2κO^3)zirconate}

Lars Jessen, Erhardt T. K. Haupt, and Jürgen Heck*[a]

Dedicated to Professor Dr. Rainer Dieter Fischer on the occasion of his 65th birthday

Abstract: The reaction of [$CpZrCl_3(thf)_2$] with methyl 4,6-*O*-benzylidene-β-D-glucopyranoside (β-MeBGH_2, **1**) in the presence of Et_3N results in the formation of the zirconate complex [Et_3NH][$(CpZrCl)_2(\mu$-Cl)\{μ-(β-MeBG)\}$_2$] (**2**). X-ray structure analyses were performed from the ligand precursor β-MeBGH_2 **1** as well as from **2**. Compound **1** crystallizes in the monoclinic chiral space group $P2_1$. The molecules show a flat arrangement including the benzylidene protecting group, and are packed in columns. The columns are held together in pairs by the formation of hydrogen bonds between the hydroxy functions in positions 2 and 3. Compound **2** crystallizes in the orthorhombic space group $P2_12_12_1$. The β-MeBG ligands are chelating the Zr atoms through the oxygen atoms in positions 2 and 3 of the glucopyranosidato ligand revealing a 1-zircona-2,5-dioxolane moiety each; the oxygen atom in position 3 is linked to both of the Zr atoms. Additionally one chloro ligand is bridging the two Zr centers. Two terminally bound chloro ligands stick out from the two Zr atoms into a chiral U-shaped cavity constructed by the two β-MeBG ligands. The cavity incorporates the tertiary ammonium cation [Et_3NH]$^+$, which is bound to one of the terminal chloro ligands through a hydrogen bond. The inclusion of the [Et_3NH]$^+$ cation in the U-shaped cavity, even in solution, is demonstrated by NMR spectroscopic data.

Keywords: carbohydrates · supramolecular chemistry · zirconium

Introduction

Low molecular building blocks based on sugars as alcoholato ligands in classical coordination compounds have been studied more extensively in the last two decades.[1] Nonetheless the corresponding compounds containing organometallic moieties are still very rare.[2] This is a surprizing fact, since in the area of enantioselective catalysis using organometallic complexes a great deal of effort has been put into the syntheses of a plethora of chiral ligands; however, by far most of them are not derived from saccharides although just these carbohydrates seem to be very suitable starting materials because of their diverse stereo information.[3] Indeed, some catalytic reactions of organometallic complexes of late transition metals with sugar derived bisphosphinito ligands reveal very high enantiomeric excess for example the hydrocyanation of vinyl arenes[4] or the asymmetric hydrogenation of the derivatives of N-acyl dehydroamino acids[5] which was applied for the industrial synthesis of L-dopa until 1990.[6]

First of all, our interest in this research topic is focussed on the coordination capability of positions 2 and 3 of pyranose sugars in organometallic complexes of early transition metals as Ti[7] and Zr. As a next step the application of these organometallic complexes in catalytic C,C coupling reactions is intended.

The chelation of a metal ion with the oxygen atoms in positions 2 and 3 of a pyranose ligand forms a 1-metalla-2,5-dioxolane ring. The stability of the ring will depend strongly on the dihedral angle of the chelating unit O2-C2-C3-O3, which flexibility is limited by the anellated pyranose ring. The emerging ring strain upon changing this dihedral angle may be the reason, why the formation of a 1-titana-2,5-dioxolane structure fails in the reaction of $CpTiCl_3$ with a glucopyranoside which was protected in position 1, 4, and 6. Without exception the glucopyranoside forms a diolato bridge between two Ti complex moieties.[7,8] Presumably, the dihedral angle O2-C2-C3-O3 of the glucopyranoside ligand, wherein the oxygen atoms are in a bisequatorial *trans* position, is too large to chelate a small Ti^{IV} ion. Only very few examples of a

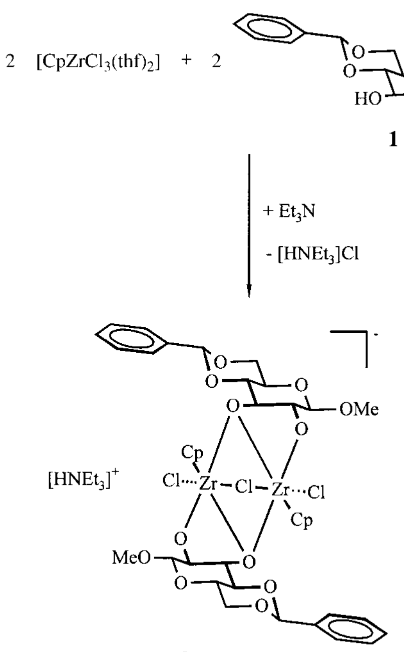
---

[a] Prof. Dr. J. Heck, Dr. L. Jessen, Dr. E. T. K. Haupt
Institut für Anorganische und Angewandte Chemie
Martin-Luther-King-Platz 6, 20146 Hamburg (Germany)
Fax: (+49) 40 42838-6945
E-mail: heck@chemie.uni-hamburg.de

1-titana-2,5-dioxolane entity are known to date, which are structurally characterized.[9] One example is a titanocene derivative wherein the Ti atom is additionally coordinated to a pinacolato ligand. The dihedral O-C-C-O angle was determined to 47.3° only,[9b] which is about 20° smaller than the corresponding angle O2-C2-C3-O3 in methyl 4,6-*O*-benzylidene-*α*-D-glucopyranoside calculated by molecular modelling.[10] However, in the Ti complexes known, which indeed contain a 1-titana-2,5-dioxolane ring, the oxygen bearing carbon atoms of the dioxolane ring are not a part of an anellated ring system. Hence, the formation of a smaller O-C-C-O dihedral angle is possible without considerable strain. Since the ion radius of Zr^{IV} is found to be distinctly larger than for Ti^{IV},[11] we suggested that the 1-zircona-2,5-dioxolane ring could be obtained by the O2,O3 chelation of a glucopyranoside ligand in organozirconium moieties.

Results and Discussion

Synthesis: Methyl 4,6-*O*-benzylidene-*β*-D-glucopyranoside (*β*-MeBGH_2, **1**) was used as precursor for the bidentate 2,3-diolato ligand, which is easily prepared from the corresponding *β*-methyl glucopyranoside.[12] The reaction of *β*-MeBGH_2 **1** with $[CpZrCl_3(thf)_2]$ in the presence of NEt_3 yielded the water sensitive triethylammonium zirconate **2** (Scheme 1) as a dinuclear complex with two glucopyranoside units acting as 2,3-diolato ligands. The yield and purity of the product **2** depend extremely on the preparation of $CpZrCl_3$ and carefully following the reaction procedure. Slight modifications in the adding of the reagents lead to unidentified mixtures of products. The dinuclear zirconate complex **2** was fully characterized by means of elemental analysis, NMR spectroscopy, and X-ray structure determination.



2

Scheme 1. Synthesis of $[Et_3NH][(CpZrCl)_2(\mu\text{-}Cl)\{\mu\text{-}(\beta\text{-}MeBG)\}_2]$ (**2**).

Stuctural analysis: In order to get a better understanding of the influence of the structural peculiarities in 2,3-diolato glucopyranoside ligands a comparison of the structural data of the ligand precursor **1** was necessary. Since structural data for **1** were not yet available in the literature, a crystal structure determination of **1** has been performed. Compound **1** precipitates in pin-shaped, colorless crystals with the monoclinic chiral space group $P2_1$ containing two molecules in the unit cell (see Table 1). As expected, the 4,6-*O*-benzylidene protecting group induces a bisequatorial anellation of the two six-membered rings (Figure 1).[12c] Consecutively, the two

Table 1. Crystallographic Data of *β*-MeBGH_2 (**1**) and $[Et_3NH][(CpZrCl)_2(\mu\text{-}Cl)\{\mu\text{-}(\beta\text{-}MeBG)\}_2]$ (**2**).

	1	**2**
formula	$C_{14}H_{18}O_6$	$C_{44}H_{58}Cl_3NO_{12}Zr_2$
M_w	282.28	1084.71
T [K]	173(2)	173(2)
λ [pm]	154.178	71.073
Crystal system	monoclinic	orthorhombic
space group	$P2_1$	$P2_12_12_1$
a [pm]	865.6(2)	1423.0(3)
b [pm]	458.90(10)	1434.1(3)
c [pm]	1710.5(3)	2335.3(5)
β [°]	95.32(3)	
V [$\times 10^6$ pm^3]	676.5(2)	4765.(17)
Z	2	4
ρ_{calcd} [Mg m^{-3}]	1.386	1.512
μ [mm^{-1}]	0.915	0.665
F (000)	300	2230
crystal size [mm^3]	$0.3 \times 0.1 \times 0.1$	$0.3 \times 0.3 \times 0.2$
scan range [°]	2.59–72.46	1.67–28.29
index range	$-10 \leq h \leq 10$	$-18 \leq h \leq 14$
	$-5 \leq k \leq 5$	$-19 \leq k \leq 14$
	$\leq 21 \leq l \leq 21$	$-31 \leq l \leq 29$
reflections measured	3086	31518
reflections unique	2614	11709
R_{int}	0.0566	0.0205
parameters	184	631
reflections $I > 4\sigma(I)$	2569	11079
GoF[a]	1.049	1.061
$R1/wR2$ ($I > 2\sigma(I)$)[b]	0.107/0.2775	0.0204/0.0432
$R1/wR2$ (all data)[b]	0.1214/0.3492	0.0235/0.0445
resd. min/max. [e$^-$ Å^{-3}]	−0.514/0.531	−0.328/0.242

[a] GoF (goodness of fit) $= \sqrt{\frac{\sum w(F_0^2 - F_c^2)^2}{n-p}}$ (n = numbers of reflections, p = numbers of parameters). [b] $R1 = \frac{\sum \| F_0 | - | F_c \|}{\sum | F_0 |}$; $wR2 = \sqrt{\frac{\sum w(F_0^2 - F_c^2)^2}{\sum w(F_0^2)^2}}$.

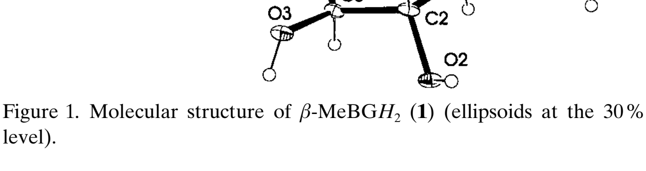


Figure 1. Molecular structure of *β*-MeBGH_2 (**1**) (ellipsoids at the 30% level).

hydroxyl groups in positions 2 and 3 gain a *trans*-bisequatorial conformation. The phenyl substituent is coplanar with the two six-membered rings. The flat arrangements of the glucopyranoside **1** enables a column-like stacking of the single molecules (Figure 2). Two columns are apparently held together by bridging hydrogen atoms between position 2 of one glucopyranoside column and position 3 of the second column. The bond lengths and angles (see Tables 2 and 3) in the solid state structure of **1** are as expected for organic compounds.

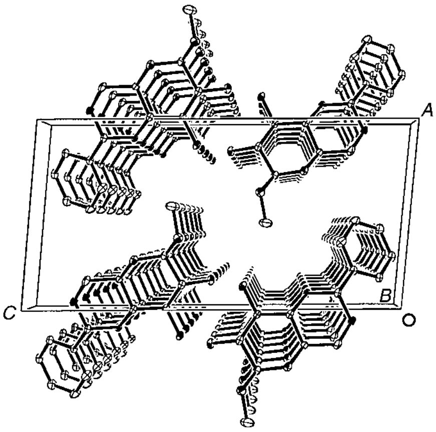


Figure 2. Stacking of the molecules of β-MeBGH_2 (**1**) in the single crystal (along *b*).

Table 2. Selected interatomic distances in β-MeBGH_2 (**1**) and $[Et_3NH][(CpZrCl)_2(\mu\text{-}Cl)\{\mu\text{-}(\beta\text{-}MeBG)\}_2]$ (**2**).

	1			**2**	
C1–C2	151.9(6)	C21–C22	152.8(2)	Zr1–O22	202.41(12)
C2–C3	152.6(7)	C22–C23	152.9(2)	Zr1–O43	213.7(5)
C3–C4	150.6(6)	C23–C24	151.2(2)	Zr1–O23	226.76(11)
C4–C5	152.1(6)	C24–C25	153.5(2)	Zr2–O42	203.9(7)
C5–C6	151.5(7)	C25–C26	151.8(2)	Zr2–O23	212.71(11)
C7–C8	149.7(7)	C27–C28	151.3(2)	Zr2–O43	225.2(7)
O1–C1	139.4(6)	C21–O21	139.4(2)	Zr1–Cl1	255.68(6)
O1–C14	142.8(7)	O21–C34	143.1(2)	Zr1–Cl3	263.63(6)
O2–C2	141.7(5)	O22–C22	141.0(2)	Zr2–Cl2	249.97(7)
O3–C3	142.6(5)	O23–C23	142.2(2)	Zr2–Cl3	271.24(7)
O5–C1	143.3(6)	O25–C21	144.3(2)	Zr1···Zr2	337.41(6)
O5–C5	142.0(6)	O25–C25	142.8(2)	N···Cl1	323.3(2)
O4–C4	143.8(5)	O24–C24	143.2(2)	N···H+	89(2)
O2···O3	290.0(5)	O22···O23	262.2(2)	Cl1···H+	246(2)
O2···O3′[a]	267.6(5)			Cl2···H+	344(3)
O2···O3″[a]	280.2(5)				

[a] O3′ and O3″ denote the oxygen atoms O3 of the two facing β-MeBGH_2 molecules in the opposite β-MeBGH_2 column.

Table 3. Selected angles [°] in β-MeBGH_2 **1** and $[Et_3NH][(CpZrCl)_2(\mu\text{-}Cl)\{\mu\text{-}(\beta\text{-}MeBG)\}_2]$ (**2**).

		1	**2**
C1-O1-C14	113.8(5)	C21-O21-C34	113.59(15)
O1-C1-C2	106.6(4)	O21-C21-C22	109.26(14)
O1-C1-O5	107.3(4)	O21-C21-O25	106.77(13)
O2-C2-C1	110.3(4)	O22-C22-C21	111.92(14)
O2-C2-C3	109.7(4)	O22-C22-C23	106.96(14)
O3-C3-C2	111.8(4)	O23-C23-C22	106.27(12)
O3-C3-C4	112.1(4)	O33-C23-C24	120.18(14)
O2-C2-C3-O3[a]	64.2	O22-C22-C23-O24[a]	51.9

[a] Dihedral angle.

The structural data, which determine the chelating capability of the oxygen atoms O2 and O3, are the dihedral angle O2-C2-C3-O3, the O2-C2-C3 and O3-C3-C2 bond angles and the corresponding O–C and C–C bond lengths. The experimentally obtained dihedral angle is 64.2° and confirms the theoretical value of 66.3° calculated for the corresponding α-D-glucopyranoside derivative by means of molecular modelling.[10] Additionally, the measured and calculated nonbonding O2–O3 distances of 290.0 and 286 pm, respectively, are in good accordance to each other.

The Zr complex **2** crystallizes in the orthorhombic space group $P2_12_12_1$ (Table 1) with four formula units. The most eye-catching overall structural feature of **2** is the U-shaped cavity. The wings of the cavity are formed by the benzylidene protected glucopyranoside moieties, which are held together by a $Cp_2Zr_2Cl_3$ building block. Thus, the cavity provides a width of 1 nm which is suitable to include the Et_3NH^+ cation (Figure 3). The $CpZr_2Cl_3O_4$ core is best described as a distorted face sharing bioctahedral comprising a Zr_2O_2Cl bicycle of two four-membered rings and two anellated ZrC_2O_2 five-membered rings (Figure 4).

The oxygen atoms in position 3 of the glucopyranosidato ligands are bridging the two Zr atoms, whereas the oxygen atoms in position 2 and two chloro ligands Cl1 and Cl2 which stick into the cavity, are bound terminally. The Zr–O and

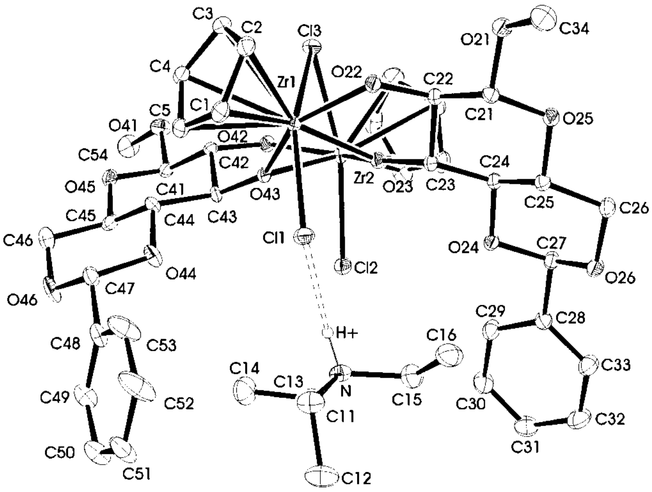


Figure 3. Molecular structure of $[Et_3NH][(CpZrCl)_2(\mu\text{-}Cl)\{\mu\text{-}(\beta\text{-}MeBG)\}_2]$ (**2**) in the crystal (the disordered β-MeBG ligand, which is calculated to 19.6%, is omitted (see Figure 9); the hydrogen atoms are omitted for clarity except the nitrogen-bound hydrogen, ellipsoids at the 30% level).

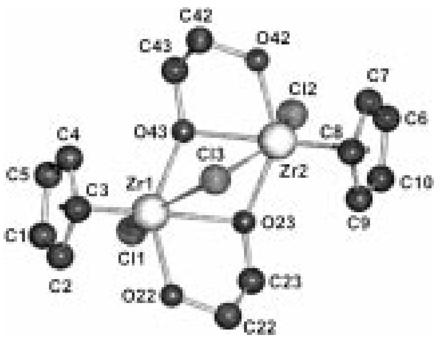


Figure 4. Schakal[27] presentation of the $Cp_2Zr_2Cl_3O_4$ core of the zirconate complex **2** illustrating the face-sharing bioctahedral arrangement.

Zr–Cl bond lengths are comparable to those recently published for CpZr complexes containing Zr–Cl and Zr–O bonds.[13–17]

The structure of the $(CpZrCl)_2(\mu\text{-}Cl)$ entity of **2** very much resembles the corresponding unit in $[Et_3NH][(\eta^5\text{-}Cp^*ZrCl)_2\text{-}(\mu\text{-}Cl)(\mu\text{-}3,5\text{-}Me_2\text{-}dpbd\text{-}1{:}2\kappa O^1,2\kappa O^2)_2]$ (**3**) (3,5-Me_2dpbdH_2 = 1,4-bis(3,5-dimethylphenyl)butan-2,3-diol).[18] The most remarkable difference is observed for the dihedral angles of the coordinating vicinal dioxo functions which are almost 0° in **3** due to the free rotation between C2–C3 of the butane backbone, whereas in **2** the dihedral angle O2-C2-C3-O3 amounts to 51.9° and 53.3° caused by the anellated, riged glucopyranose ring.

The complexes **2** and **3** illustrate an interesting Zr–Cl bond alternation. In **2** the terminal Zr–Cl bonds are distinctly different from each other: Zr1–Cl1 255.68(6) versus Zr2–Cl2 249.97(7) pm. A comparable asymmetry in the $(CpZrClO_2)_2\text{-}(\mu\text{-}Cl)$ core is found for **3**, and is assumed as a result of the hydrogen bond to the counterion $[Et_3NH]^+$ which we were able to analyze by means of the structure determination of **2**.

The position of the nitrogen-bound hydrogen atom in the $[Et_3NH]^+$ cation was calculated from residual electron density, and was refined without restriction. The resulting distances between the hydrogen and the nitrogen atom and chlorine atom Cl1 are 89(2) pm and 246(2) pm, respectively. It is noteworthy that the NHCl triple in **2** is not linear arranged but encloses an angle of 145(2)°. The nonbonding distance between N and Cl1 amounts to 323.3(2) pm, and is slightly longer than the corresponding N–Cl distance in $[Et_3NH]Cl$ (310.7 pm).[19] The elongation of the N···Cl1 distance in **2** compared with free $[Et_3NH]Cl$ may be explained by the interaction of the proton with the Zr-bound chloro ligand in **2**, whereas in $[Et_3NH]Cl$ the hydrogen bonding occurs with a free chloride anion.

The hydrogen bond to the chloro ligand Cl1 causes a diminution of the Zr1–Cl1 bonding interaction resulting in a Zr1–Cl1 bond lengthening compared with the Zr2–Cl2 bond. Subsequently, the Zr1–Cl3 bond, which is in *trans* position to the Zr1–Cl1 bond, will become shorter, as it is found in the crystal structure of **2** (see Table 2).

The localization of the bridging hydrogen only between N and Cl1 is corroborated by the long $H^+\cdots Cl2$ distance of 344(3) pm, which is about 100 pm longer than $H^+\cdots Cl1$ 246(2) pm. The $[Et_3NH]^+$ cation is slightly distorted from an ideal trigonal pyramidal structure: the proton is somewhat tilted towards Cl1 illustrated by the angle Cl1-N-H of 103.3(1.4)°, whereas the angle C15-N-H increases to 110.1(1.4)°; the anlge C13-N-H lies in between (105.1(1.4)°).

The structural data of the β-MeBG ligand in **2** very much resemble those of the ligand precursor β-MeBGH_2 (**1**) as easily seen in Figure 5, which illustrates a superposition of the β-MeBG entities of **1** and **2**. The only larger structural deviation is observed for the dihedral angle O2-C2-C3-O3 which decreases from 64.2° to 51.9° and 53.3°, respectively, on going from **1** to **2**. Simultanously, the bond angles O2-C2-C3 and O3-C3-C2 change from 109.7(4) and 111.8(4) in **1** to 107.0(1) and 106.3(1) or 105.6(4) and 108.7(4), respectively, in **2**. Therefore, the nonbonding distance O2···O3 decreases almost 30 pm from 290.0 pm in β-MeBGH_2 (**1**) to 262.2 pm in the β-MeBG ligand of **2**.

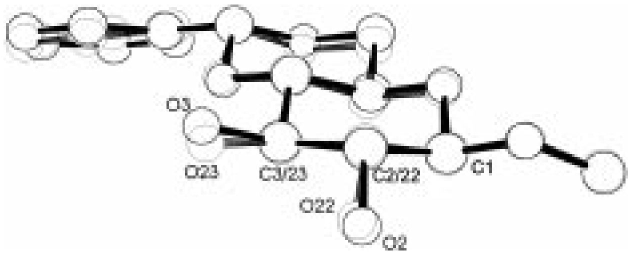


Figure 5. Superposition of the structures of β-MeBGH_2 (**1**) and of the non-disordered β-MeBG ligand in **2** (hydrogen atoms are omitted for clarity).

NMR studies: The NMR spectra obtained from CD_2Cl_2 or $CDCl_3$ solutions, indicate an overall molecular symmetry according to the point group C_2 for the zirconate anion. Interesting features of **2** in solution can be stated from the ^1H NMR studies concerning the proton resonance signals of the $[Et_3NH]^+$ cation. The shift of the resonance signals depends on the concentration of free $[Et_3NH]Cl$: the signal of nitrogen-bound proton of a pure sample of $[Et_3NH]Cl$ is observed at $\delta = 11.9$, whereas the pure sample of **2** reveals the corresponding signal at $\delta = 7.13$. In Figure 6 the NMR shift of the ammonium proton signal is depicted as a function of the mol fraction of $[Et_3NH]Cl$. To a lesser extend but also significantly the resonance signals of the methylene and methyl protons of the ethyl substituents are high-field shifted with decreasing concentration of free $[Et_3NH]Cl$ (Figure 7).

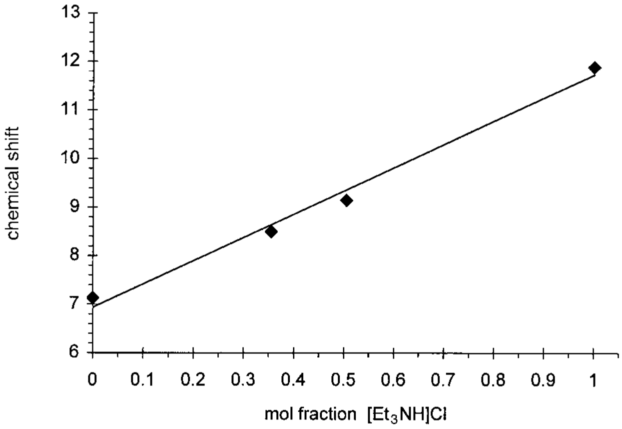


Figure 6. Chemical shift of the signal of the nitrogen-bound hydrogen atom as a function of the mol fraction of $[Et_3NH]Cl$.

The increased high-field shift of the averaged signals with less amount of additional ammonium cation in the solution of the zirconate complex **2** is a clear indication for the exchange of free and zirconate bound $[Et_3NH]^+$. The high-field shift of the ethyl proton signals upon inclusion into the zirconate cavity is explained by the molecular structure of **2** in Figure 3. The ethyl substituents are situated in the shielding area of the anisotropy cone of the phenyl rings. The inclusion of the $[Et_3NH]^+$ cation in the chiral cavity of the zirconate anion is also confirmed by variable temperature ^1H NMR experiment (Figure 8).

The spectrum at room temperature contains a well resolved multiplet for the methylene protons; the multiplet can

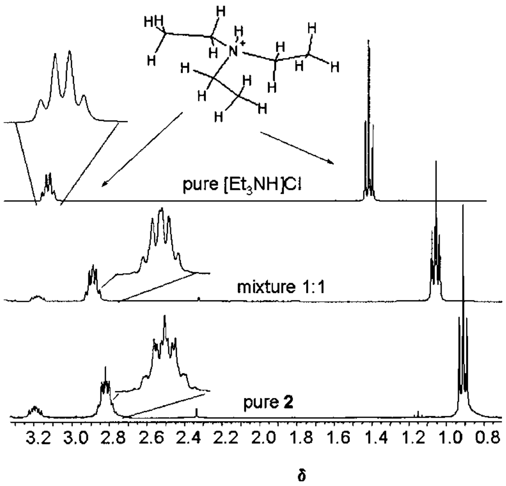


Figure 7. ^{1}H NMR spectra of the Et region of the zirconate complex **2** with different amounts of [Et$_3$NH]Cl (solvent: CDCl$_3$)

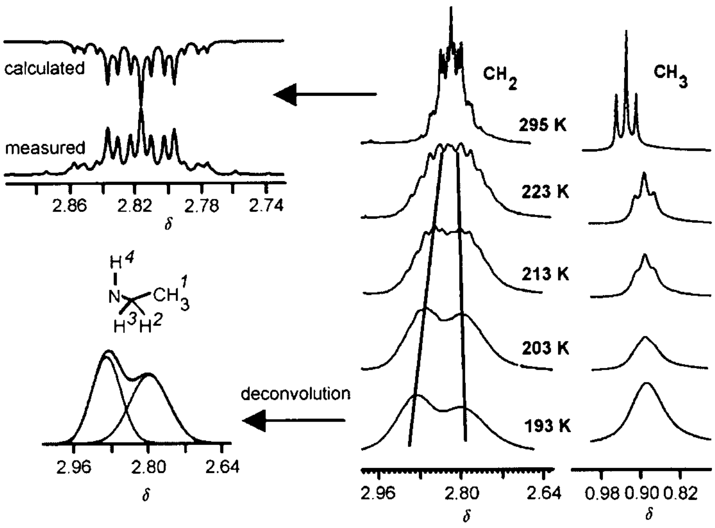


Figure 8. Variable temperature ^{1}H NMR spectra illustrating the increasing anisochrony of the methylene protons with decreasing temperature. The upper insert demonstrates the experimental and calculated signal for the CH$_2$ group of the Et substituent (coupling constants in Hz: H1,H2 = 7.27; H1,H3 = 7.33, H2,H3 = 6.05, H2,H4 = −10.58, H3,H4 = 0.50); the resolution of the experimental signal for the methylene protons is mathematically enhanced. The lower insert shows the deconvolution of the methylene signal at 193 K.

satisfactory be simulated only by taking into account two different methylene protons, which resonance frequencies are incidentally isochronic at room temperature, but couple differently to the ammonium proton (see insert, Figure 8). Upon lowering the temperature to 193 K the resonance signals of the methylene protons successively turn anisochronic whereas the methyl protons still show one signal. A deconvolution of the two broad signals at $\delta = 2.80$ and 2.89 proves the 1:1 ratio of the two methylene protons. The different intensities and line widths due to the different coupling constants between the methylene protons and the ammonium proton (Figure 8). The inclusion of the [Et$_3$NH]$^+$ in the chiral zirconate cavity prevents the inversion at the nitrogen atom providing a diastereotopic interaction of the methylene protons with the chiral cavity.

Conclusion

The reaction of [CpZrCl$_3$(thf)$_2$] in the presence of NEt$_3$ with the selectively protected glucopyranoside β-MeBGH_2 (**1**), which contains two hydroxyl functions in positions 2 and 3, reveals the first CpZr-glucopyranosidato complex **2** as a dinuclear zirconate. In **2** a chiral U-shaped cavity is formed which includes the [Et$_3$NH]$^+$ counterion in the solid state and even in solution. A fast exchange of the [Et$_3$NH]$^+$ cation is observed in the presence of [Et$_3$NH]Cl. The stability of **2** in a supramolecular arrangement on the one side and the possibility of cation exchange on the other side makes **2** a very promising candidate for chiroselective recognition[20] for example for protonated chiral amines, which is subject of current work.

An important outcome of the X-ray structure analysis of **2** is the formation of a 1-zircona-2,5-dioxolane entity with an anellated glucopyranoside, demonstrating the chelating ability of the oxygen atoms in positions 2 and 3 of the glucopyranosidato ligand. However, the dihedral angle O2-C2-C3-O3 is decreasing upon coordination in **2** from 64.2° in free β-MeBGH_2 **1** to 51.9° and 53.3°, which may cause some strain in the glucopyranoside ring. Considering the coordination of the much smaller Ti^{IV} ion by the chelating vicinal dioxofunction much stronger ring strain would be effected, thus preventing the formation of a 1-titana-2,5-dioxolane moiety with chelating glucopyranosidato ligands. To the best of our knowledge only one mononuclear organotitanium complex with 1-titana-2,5-dioxolane moiety has structurally been characterized to date.[9b] In this case the 1,1-bis(η^5-cyclopentadienyl)-3,4-diphenyltitanadioxolane illustrates a still smaller dihedral anlge O-C-C-O of 47.3° but extraordinary long Ti–O bond lengths of 189.2 and 190.3 pm, respectively, whereas most of the Ti–O bond lengths range between 175 and 180 pm.[21] The general influence of the size of cations and the shape and flexibility of coordinating sugar ligands on the strength of complexes has already been shown conclusively for the interaction of polyols with lanthanides.[22]

Experimental Section

General methods: All experiments were carried out under purified nitrogen atmosphere. All solvents were vigorously dried and freshly distilled under nitrogen. NMR: Bruker AM 360 and Varian Gemini 2000BB. Elemental analysis: Heraeus CHN-O-Rapid, Institut für Anorganische und Angewandte Chemie, Universität Hamburg. β-MeBGH_2 **1**[12] and [CpZrCl$_3$(thf)$_2$][23] were synthesized according the literature.

Triethylammonium μ-chloro-bis{chloro(η^5-cyclopentadienyl)(methyl 4,6-*O*-benzylidene-β-D-glucopyranosidato-1κ*O*^{2},1:2κ*O*^{3}-zirconate} (2): A solution of NEt$_3$ (1.02 mL, 7.33 mmol) in THF (20 mL) was added to [CpZrCl$_3$(thf)$_2$] (595 mg, 1.47 mmol) dissolved in THF (40 mL). After stirring at room temperature for 1 h a solution of **1** (415 mg, 1.47 mmol) in THF (20 mL) was added dropwise. The reaction mixture was stirred for 14 h at room temperature, the precipitated [Et$_3$NH]Cl was filtered off and the filtrate was evaporated to dryness. The residue was washed several times with small portions of diethyl ether and toluene until the solution was colorless. The title compound was obtained as a light beige microcrystalline solid (674 mg, 85 %). M.p. 210 °C (decomp); ^{1}H NMR (360 MHz, CD$_2$Cl$_2$, 25 °C, TMS): $\delta = 7.8$ (m, 4H, phenyl$_{\text{meta-H}}$), 7.3 (m, 6H, phenyl$_{\text{ortho-H/para-H}}$), 6.9 (s, 10H, Cp), 5.7 (s, 2H, CH$_{\text{benzylidene}}$), 4.7 (dd, ^3J(H3,H2) = 10, ^3J(H3,H4) = 10 Hz, 2H, H3), 4.4 (dd, ^3J(H6eq,H6ax) = 11, ^3J(H6eq,H5) =

5 Hz, 2H, H6$_{eq}$), 4.2 (d, ^3J(H1,H2) = 8 Hz, 2H, H1), 4.0 (dd, ^3J(H4,H5) = 9 Hz, 2H, H4), 3.9 (dd, ^3J(H6ax,H5) = 10 Hz, 2H, H6$_{ax}$), 3.8 (dd, 2H, H2), 3.5 (s, 6H, OMe), 3.2 (ddd, 2H, H5), 2.9 (m, 6H, $CH_{2(NEt_3)}$), 1.1 (t, ^3J(H$_{methyl}$,H$_{methylene}$) = 7 Hz, 9H, $CH_{3(NEt_3)}$); ^{13}C NMR (50 MHz, CD_2Cl_2, 25 °C, TMS): δ = 130, 128, 126 (phenyl), 118 (Cp), 106 (C1), 101 (C7), 86 (C3), 85 (C2), 82 (C4), 74 (C6), 72 (C5), 60 (OMe), 47 ($CH_{2(NEt_3)}$), 12 ($CH_{3(NEt_3)}$); elemental analysis calcd (%) for $C_{44}H_{58}Cl_3NO_{12}Zr_2$ (1081.74): C 48.85, H 5.40, N 1.29; found: C 48.69, H 5.62, N 1.54.

X-ray structure determinations: Suitable crystals for X-ray structure analysis were obtained for **1** by slow evaporation of a concentrated $CDCl_3$ solution of **1**. The data for **1** were collected on a four circle diffractometer with $Cu_{K\alpha}$ irradiation (ENRAF Nonius, CAD 4). The structure was solved by direct methods.[24] Refinement on F^2 were carried out by full-matrix least square techniques.[25] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a fixed isotropic thermal parameter related by a factor of 1.2 to the value of the equivalent isotropic thermal parameter of their carrier atoms. Weights are optimized in the final refinement cycles (Table 1).

Suitable crystals of **2** for X-ray structure analysis were obtained from slow diffusion of the diethyl ether to a saturated solution of **2** in a mixture of toluene/THF (1:1). The data for **2** were collected on a four-circle diffractometer with $Mo_{K\alpha}$ irradiation (Hilger&Watts, Y240). The solution of the crystal structure was performed in accordance to **1**, with the exception of the N bound hydrogen atom. Its position was calculated from residual electron density and was refined without restriction. The structural analysis was hampered by a diffuse incorporation of solvent molecules such as toluene, THF and diethyl ether in the single crystal, which induce a slight disorder. The best structure solution was obtained by taking into account a disorder in one of the two β-MeBG ligands to a portion of 19.6% (Figure 9). To the same amount a cavity of about 160×10^6 pm^3 can be calculated in the unit cell;[26] this cavity is large enough to encapsulate a solvent molecule such as diethyl ether, toluene or THF, which was proven by a NMR sample of the same crystalline material. The cavity contains a residual electron density, which can sufficienty refined by the assumption of one carbon atom; the alternative assumption of a water molecule is excluded because of the sensitivity of **2** against moisture. For more details see Table 1.

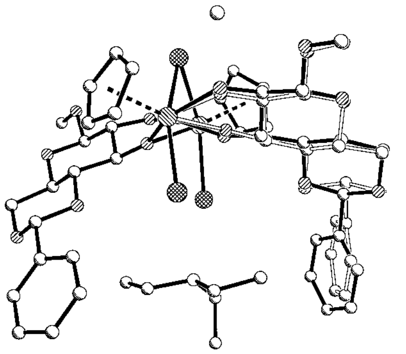


Figure 9. Molecular structure of $[Et_3NH][(CpZrCl)_2(\mu\text{-}Cl)\{\mu\text{-}(\beta\text{-}MeBG)\}_2]$ (**2**) in the crystal illustrating the disordered β-MeBG ligand (on the right, open lines), which is calculated to a portion of 19.6%. To the same amount a cavity of about 160×10^6 pm^3 can be calculated in the unit cell.[26] It contains a residual electron density, which can sufficiently refined by the assumption of one carbon atom (for more details see Experimental Section. The carbon atom represents the diffuse incorporated solvent molecules, which are proven by NMR spectroscopy (the hydrogen atoms are omitted for clarity).

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft (DFG, HE 1309/4-1) and by the Fonds der Chemischen Industrie.

[1] Y. E. Alekseev, A. D. Garnovskii, Y. A. Zhdanov, *Russ. Chem. Rev.* **1998**, *67*, 649–669; S. Yano, *Coord. Chem. Rev.* **1988**, *92*, 113–156; U. Piarulli, C. Floriani, *Prog. Inorg. Chem.* **1997**, *45*, 393–429; J.-F. Verchère, S. Chapelle, F. Xin, D. C. Crans, *Prog. Inorg. Chem.* **1998**, *47*, 837–945; S. J. Angyal, *Chem. Soc. Rev.* **1980**, *9*, 415–428; S. J. Angyal, *Adv. Carbohydr. Chem. Biochem.* **1989**, *47*, 1–43; M. Klaassen, P. Klüfers, *Z. Anorg. Allg. Chem.* **1994**, *620*, 1631–1634; J. Burger, C. Gack, P. Klüfers, *Angew. Chem.* **1994**, *107*, 2950–2951; *Angew. Chem. Int. Ed. Engl.* **1994**, *34*, 2947–2949; J. Burger, P. Klüfers, *Chem. Ber.* **1995**, *128*, 75–79; P. Klüfers, J. Schuhmacher, *Z. Anorg. Allg. Chem.* **1995**, *621*, 19–22; P. Klüfers, P. Mayer, J. Schuhmacher, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1373–1379; J. Burger, P. Klüfers, *Z. Anorg. Allg. Chem.* **1996**, *622*, 1740–1748; P. Klüfers, P. Mayer, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1496–1498; J. Burger, P. Klüfers, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1547–1554; P. Klüfers, P. Mayer, *Acta Crystallogr. Sect. C* **1998**, *54*, 583–586; J. Burger, P. Klüfers, *Z. Anorg. Allg. Chem.* **1998**, *624*, 359–360.

[2] a) M. Riediker, R. O. Duthaler, *Angew. Chem.* **1989**, *101*, 488–490; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 494–495; G. Bold, R. O. Duthaler, M. Riediker, *Angew. Chem.* **1989**, *101*, 491–493; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 497–499; M. Riediker, A. Hafner, U. Piantini, G. Rihs, A. Togni, *Angew. Chem.* **1989**, *101*, 493–495; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 498–500; K. Oertle, H. Beyeler, R. O. Duthaler, W. Lottenbach, M. Riediker, E. Steiner, *Helv. Chim. Acta* **1990**, *73*, 353–358; R. O. Duthaler, A. Hafner, M. Riediker, *Pure Appl. Chem.* **1990**, *62*, 631–642; R. O. Duthaler, A. Hafner, P. L. Alsters, G. Bold, G. Rihs, P. Rothe-Streit, B. Wyss, *Inorg. Chim. Acta* **1994**, *222*, 95–113; U. Piarulli, C. Floriani, N. Re, G. Gervasio, D. Viterbo, *Inorg. Chem.* **1998**, *37*, 5142–5148; b) D. Steinborn, H. Junicke, C. Bruhn, *Angew. Chem.* **1997**, *109*, 2803–2805; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2686–2688; H. Junike, C. Bruhn, D. Ströhl, R. Kluge, D. Steinborn, *Inorg. Chem.* **1998**, *37*, 4603–4606; H. Junike, C. Bruhn, R. Kluge, A. S. Serianni, D. Steinborn, *J. Am. Chem. Soc.* **1999**, *121*, 6232–6241; c) J.-M. Beau, T. Gallagher, *Top. Curr. Chem.* **1997**, *187*, 1–43; d) J. D. Donaldson, S. M. Grimes, L. Pellerito, M. A. Girasolo, P. J. Smith, A. Cambria, M. Famà, *Polyhedron* **1987**, *6*, 383–386; K. Burger, L. Nagy, N. Buzás, A. Vértes, H. Mehner, *J. Chem. Soc. Dalton Trans.* **1993**, 2499–2504; G. Hodosi, P. Kovác, *Carbohydr. Res.* **1997**, *303*, 293–243; A. J. Crowe, P. J. Smith, *J. Organomet. Chem.* **1976**, *110*, C57–C59; C. Cruzado, M. Barnabé, M. Martin-Lomas, *J. Org. Chem.* **1989**, *54*, 465–469, A. F. Husain, R. C. Poller, *J. Organomet. Chem.* **1976**, *118*, C11–C12; K. H. Dötz, D. Paetsch, H. Le Bozec, *J. Organomet. Chem.* **1999**, *589*, 11–20.

[3] H. Kunz, *Pure Appl. Chem.* **1995**, *67*, 1627–1635.

[4] T. V. RajanBabu, A. L. Casalnuovo, *J. Am. Chem. Soc.* **1992**, *114*, 6265–6265.

[5] R. Selke, H. Pracejus, *J. Mol. Cat. A* **1986**, *37*, 213–225; R. Selke, *J. Prakt. Chem.* **1987**, *329*, 717–724; R. Selke, *J. Organomet. Chem.* **1989**, *370*, 241–248; R. Selke, *J. Organomet. Chem.* **1989**, *370*, 249–256; R. Selke, C. Facklam, H. Foken, D. Heller, *Tetrahedron*: *Asymmetry* **1993**, *4*, 369–382; U. Berens, C. Fischer, R. Selke, *Tetrahedron*: *Asymmetry* **1995**, *4*, 1105–1108; M. Michalik, T. Freier, M. Schwarze, R. Selke, *Magn. Reson. Chem.* **1995**, *33*, 835–840; D. Heller, S. Borns, W. Baumann, R. Selke, *Chem. Ber.* **1996**, *129*, 85–89; R. Selke, M. Ohff, A. Riepe, *Tetrahedron* **1996**, *52*, 15079–15102; R. Kadyrov, D. Heller, R. Selke, *Tetrahedron*: *Asymmetry* **1998**, *9*, 329–340.

[6] W. Vocke, R. Hänel, F.-U. Flöther, *Chem. Tech.* (*Leipzig*) **1987**, *39*, 123–125.

[7] L. Jessen, J. Heck, in: *Chemie Nachwachsender Rohstoffe*, Bundesministerium für Umwelt, Jugend und Familie, **1997**, 79–82.

[8] L. Jessen, *Dissertation*, Universität Hamburg, **2000**.

[9] a) C. A. Zechmann, J. C. Huffman, K. Folting, K. G. Caulton, *Inorg. Chem.* **1998**, *37*, 5856–5861; b) R. Kempe, A. Spannenberg, N. Peulecke, U. Rosenthal, *Z. Kristall.–New Crystallogr. Struct.* **1998**, *213*, 425–425.

[10] B. Zhang, S. Zhang, K. Wang, *J. Chem. Soc. Dalton Trans.* **1996**, 3257–3263.

[11] U. Müller, in *Anorganische Strukturchemie* (Eds.: C. Elschenbroich, F. Hensel, H. Hopf), Teubner, Stuttgart, **1991**, p. 44.

[12] a) A. N. de Belder, *Adv. Carbohydr. Chem.* **1965**, *20*, 219–302; A. N. de Belder, *Adv. Carbohydr. Chem. Biochem.* **1977**, *34*, 179–241; b) M. E. Evans, *Carbohydr. Res.* **1972**, *21*, 473–475; M. E. Evans,

Meth. Carbohydr. Res. **1980**, *8*, 313–315; c) J. Lehmann, in *Kohlenhydrate, Chemie und Biologie*, Thieme, Stuttgart, New York, **1996**, p. 101.

[13] a) G. Erker, K. Kropp, J. L. Atwood, W. E. Hunter, *Organometallics* **1983**, *2*, 1555–1561; b) L. M. Engelhardt, R. I. Papasergio, C. L. Raston, A. H. White, *Organometallics* **1984**, *3*, 18–20; c) R. M. Waymouth, B. D. Santasiero, R. J. Coots, M. J. Bronikowski, R. H. Grubbs, *J. Am. Chem. Soc.* **1986**, *108*, 1427–1441.

[14] a) F. A. Cotton, M. P. Diebold, P. A. Kibala, *Inorg. Chem.* **1988**, *27*, 799–804; b) S. Ciruelos, T. Cuenca, R. Gómez, P. Gómez-Sal, A. Manzanero, P. Royo, *Polyhedron* **1998**, *17*, 1055–1064.

[15] a) L. M. Babcock, V. W. Day, W. G. Klemperer, *J. Chem. Soc. Chem. Commun.* **1988**, 519–520; b) R. Bortolin, V. Patel, I. Munday, N. J. Taylor, A. J. Carty, *J. Chem. Soc. Chem. Commun.* **1985**, 456–458; c) M. Bochmann, S. J. Lancaster, M. B. Hursthouse, M. Mazid, *Organometallics* **1993**, *12*, 4718–4720.

[16] a) G. Hidalgo, M. A. Pellighelli, P. Royo, R. Serrano, A. Tiripicchio, *J. Chem. Soc. Chem. Commun.* **1990**, 1118–1120; b) U. Hagenau, *Dissertation* Universität Hamburg, **1997**; c) U. Hagenau, J. Heck, W. Kaminsky, A.-M. Schauwienold, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1814–1821.

[17] B. Galeffi, M. Simard, J. D. Wuest, *Inorg. Chem.* **1990**, *29*, 955–958.

[18] D. L. Clark, D. R. Click, S. K. Grumbine, B. L. Scott, J. G. Watkin, *Inorg. Chem.* **1998**, *37*, 6237–6243.

[19] M. A. James, T. S. Camron, O. Knop, M. Neuman, M. Falk, *Can. J. Chem.* **1985**, *63*, 1750–1758.

[20] F. Vögtle in *Supramolekulare Chemie* (Eds.: C. Elschenbroich, F. Hensel, H. Hopf), Teubner, Stuttgart, **1989**, p. 61 and p. 176; J.-M. Lehn in *Supramolecular Chemistry*, *Concepts and Perspectives*, VCH, Weinheim, **1995**, p. 26; R. Dharanipragada, S. B. Ferguson, F. Diederich, *J. Am. Chem. Soc.* **1988**, *110*, 1679–1690; M. Pietraszkiewicz, N. Spencer, *J. Coord. Chem.* **1992**, *27*, 115–127.

[21] a) J. C. Huffman, K. G. Moloy, K. G. Caulton, *Inorg. Chem.* **1988**, *27*, 2190–2192; b) J. C. Huffman, K. G. Moloy, J. A. Marsella, K. G. Caulton, *J. Am. Chem. Soc.* **1980**, *102*, 3009–3014; c) R. O. Duthaler, P. Herold, W. Lottenbach, K. Oertle, M. Riediker, *Angew. Chem.* **1989**, *101*, 490–491; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 496–497; d) R. O. Duthaler, A. Hafner, *Chem. Rev.* **1992**, *92*, 807–832.

[22] S. J. Angyal, *Aust. J. Chem.* **2000**, *53*, 567–570; S. J. Angyal, D. C. Craig, *Carbohydr. Res.* **1994**, *241*, 1–8.

[23] G. Erker, C. Sarter, M. Albrecht, S. Dehnicke, C. Krüger, E. Raabe, R. Schlund, R. Benn, A. Rufinska, R. Mynott, *J. Organomet. Chem.* **1990**, *382*, 89–102.

[24] G. M. Sheldrick, SHELXS-86, Program for Structure Solution, Universität Göttingen, **1986**.

[25] G. M. Sheldrick, SHELXL-86, Program for Structure Refinement, Universität Göttingen, **1986**.

[26] Calculated with the program PLATON, A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, C34.

[27] E. Keller, Schakal 97, Universität Freiburg, **1997**.

Received: April 10, 2001 [F3192]