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Structural Consequences in α- and β-Glucopyranosidato Complexes of Cp*TiCl$_3$

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Dedicated to Professor Dr. Christoph Elschenbroich on the occasion of his 70th birthday

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The reaction of methyl-4,6-*O*-(naphthyl-2′-methylidene)-α-D-glucopyranoside (α-MeNGH_2) with trichloridopentamethylcyclopentadienyltitanium [Cp*TiCl$_3$] and triethylamine in toluene reveals the dinuclear complex [(Cp*TiCl)-μ-(α-MeNG)]$_2$ (**2**). Complex **2** was characterized by elemental analysis, ^{1}H and ^{13}C NMR spectroscopy, circular dichroism, as well as single-crystal structure analysis. Compared to the complex with the β-anomer of the ligand in [(Cp*TiCl)-μ-(β-MeNG)]$_2$ (**1**), it is obvious that the absolute configuration of the Ti atoms in **2** have changed.
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Introduction

Our interest in the organometallic chemistry of the early transition metal Ti with monosaccharide ligands has led to the previously reported reactions of methyl-4,6-*O*-benzylidene-β-D-glucopyranoside (β-MeBGH_2)[1] and methyl-4,6-*O*-(naphthyl-2′-methylidene)-β-D-glucopyranoside (β-MeNGH_2)[2,3] with organotitanium complexes.[4] The reactions of these monosaccharides with [Cp*TiCl$_3$] and triethylamine resulted in the formation of dinuclear titanium complexes with two bridging glucopyranosidato ligands. An X-ray structure analysis revealed a dinuclear complex illustrating a unique C_2 symmetric chiral molecular pocket, which can be seen from the molecular structure of the naphthyl derivative **1** (Figure 1).

In order to confine the space around the titanium atoms for possible stereoselective reaction, attempts were made to introduce the α-anomer of the glucopyranosidato ligand in Ti complexes of type **1**.

Results and Discussion

Synthesis

The reaction of α-MeNGH_2 with [Cp*TiCl$_3$] was carried out in toluene in the presence of triethylamine (Scheme 1) according to the synthesis of the dinuclear complexes of the β-anomer.[4]

We obtained the yellow dinuclear complex (*T*-4-*R*;*T*-4-*R*)-methyl-4,6-*O*-(naphthyl-2′-methylidene)-α-D-glucopyranosidato-1(κO^2,2κO^3)-[methyl-4,6-*O*-(naphthyl-2′-methylidene)-α-D-glucopyranosidato-1κO^3,2κO^2]bis[chlorido(η^5-pentamethylcyclopentadienyl)titanium(IV)] (**2**) (Figure 2) in good yields.[5]

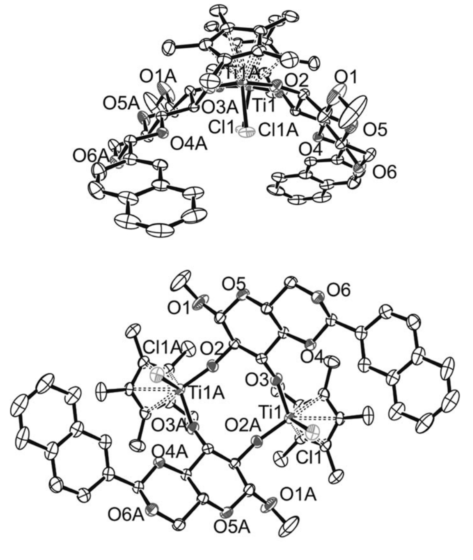
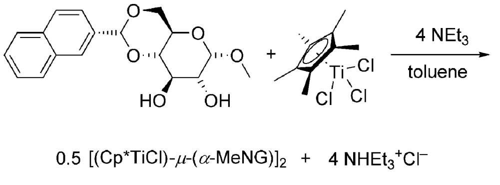


Figure 1. ORTEP drawings of the molecular structure of **1** in the crystal. Thermal ellipsoids with 50% probability at 153 K (hydrogen atoms omitted for clarity).[4]



Scheme 1. Synthesis of **2**.

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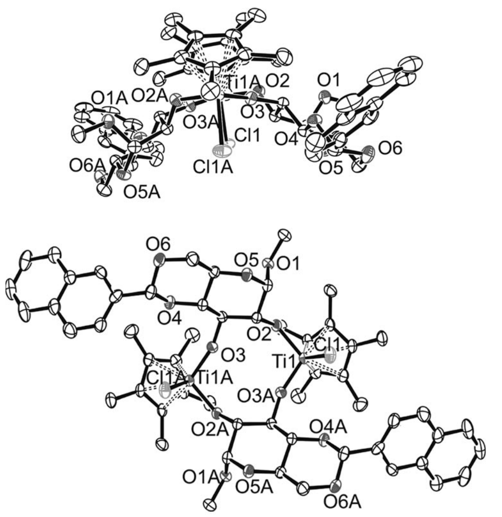

Figure 2. ORTEP drawings of the molecular structure of **2** in the crystal. Thermal ellipsoids with 50% probability at 103 K (hydrogen atoms omitted for clarity). 23% of the naphthyl groups are disordered.

^{1}H NMR spectra of the crude reaction products revealed the formation of additional complexes, which, however, could not yet be isolated and characterized. When the reaction is performed under different conditions or with different stoichiometry, it only results in different yields of the stable dinuclear complex **2**.

Molecular Structure

Compound **2** crystallizes in the space group *C*2, *Z* = 2, R_1 = 0.0389.[6] Both titanium atoms are bridged via two vicinal diolato functions of the glucopyranosidato ligands, forming a dititana ten-membered ring. The dihedral angle O2–C2–C3–O3 of **2** is 66.59°. This value varies only marginally from 66.42° obtained for **1** (Table 1). Compared to the structure of the β-derivative **1** (Figure 1),[7] it becomes obvious that the absolute configuration at the titanium atoms has changed from *T*-4-*S* in **1** to *T*-4-*R* in **2**.

It is worthwhile to note that all of the known cyclopentadienyl-2,3-pyranosidato titanium complexes are dinuclear with bridging monosaccharide ligands; no hint was found for a chelating coordination mode of the 2,3-diolato function. The absence of any chelating coordination is most probably due to the small radius of the Ti^{IV} ion (56 pm)[8] and the rather inflexible conformation of the cyclic monosaccharide ligands, demonstrated by the O2–C2–C3–O3 dihedral angle of about 60 ± 6° regardless of whether the ligand is free or coordinated. Even when allopyranosidato ligands with a *cis* orientation of the 2,3-diolato coordination site are used, wherein the O2–C2–C3–O3 dihedral angle of the free ligands is 55.5°, only a dinuclear complex with a bridging pyranosidato ligand is found.[9] When the radius of the metal ion increases from Ti^{IV} (56 pm) to Zr^{IV} (86 pm),[8] a mixed bridging and chelating mode of the 2,3-diolato monosaccharide ligands is obtained.[10] Moreover, when 2,3-diamino-functionalized monosaccharides are coordinated to larger metal atoms, e.g., in a low oxidation state, such as Cr^0 (125 pm), Mo^0 (136 pm) and W^0 (137 pm),[8] a chelating coordination is exclusively found.[11]

Table 1. Selected bond lengths [pm] and bond angles [°] for **1** and **2**. Calculated nonbonding distances are represented by dots (···). Standard deviations are given in parentheses.

Bond/Angle	Compound **1**	Compound **2**
Ti1–Cl1	230.3 (1)	231.0 (1)
Ti1–O3	181.6 (3)	178.0 (2)
Ti1A–O2	177.9 (2)	184.4 (2)
O2–C2	140.0 (4)	141.3 (3)
O3–C3	139.0 (4)	141.3 (3)
O2·········O3	286.7	291.3
O2–C2–C3–O3[a]	66.42	66.59
Ti1–O3–C3	145.6 (2)	163.3 (1)
Ti1A–O2–C2	165.9 (2)	127.0 (2)
O2A–Ti1–O3	106.0 (1)	105.8 (1)
Cl1–Ti1–O2A	98.3 (1)	101.2 (1)
Cl1–Ti1–O3	105.0 (1)	100.6 (1)

[a] Dihedral angle.

The molecular structure of **1** and **2** obeys C_2 symmetry in the solid state. Indications for the change of the coordination mode at the metal atoms in **2** relative to **1** are found for the bond lengths Ti1–O3 and Ti1A–O2 and bond angles Ti1–O3–C3 and Ti1A–O2–C2, the order of whose values inverts on going from **1** to **2**: the Ti–O bond length decreases from 181.6(3) pm to 177.9(2) pm for **1**, whereas the corresponding bond length for **2** increases from 178.0(2) pm to 184.4(2) pm. These structural changes correspond to an increase in the bond angles at the oxygen atoms on going from Ti1–O3–C3 [145.6(2)°] to Ti1A–O2–C2 [165.9(2)°] for **1** and a decrease in the corresponding bond angles of **2** altering from Ti1–O3–C3 = 163.3(2)° to Ti1A–O2–C2 = 127.0(2)°. The decrease in bond length with an increase in the related bond angle indicates an increase in the bond order of the Ti–O bond, which may be due to a growing amount of a π-donor bonding mode.[12] The different coordination modes of **1** and **2** also influence the chemical shifts in ^{1}H NMR spectroscopy. The signals of proton 1, 2 and 3 detected in the spectra of the ligand precursors α-MeNGH_2 and β-MeNGH_2 are shifted in the same order. Upon coordination with [Cp*TiCl$_3$], the signals of 2-H and 3-H are shifted to low field. Depending on the coordination modes caused by the different anomers (α-MeNGH_2 → *T*-4-*R* and β-MeNGH_2 → *T*-4-*S*), the 2-H signal of compound **2** experiences the largest shift to low field, and for compound **1** the 3-H signal experiences the largest shift to low field (Table 2).

Table 2. Chemical shifts [ppm] for signals of protons 1, 2, 3 in compounds **1**, **2**, α-MeNGH_2 and β-MeNGH_2, recorded in CDCl$_3$.

Compound	1-H	2-H	3-H
α-MeNGH_2	4.81	3.65	3.94
[(Cp*TiCl)-μ-(α-MeNG)]$_2$ (**2**)	4.69	4.73	4.61
β-MeNGH_2	4.33	3.54–3.49	3.88–3.81
[(Cp*TiCl)-μ-(β-MeNG)]$_2$ (**1**)	4.69	4.14	4.95

The different shifts of 2-H and 3-H in complexes **1** and **2** imply that an NMR spectroscopic characterization may allow the determination of the absolute configuration at the titanium atoms for this type of complexes.

Furthermore, the difference in the absolute configurations of **1** and **2** at the titanium atoms has been proved by means of circular dichroism for both complexes.[13] Compound **1** reveals a positive Cotton effect (CE)[14] at λ = 237 nm and **2** a negative CE at λ = 249 nm. An additional but opposite CE is found for **1** at λ = 278 nm (negative) and for **2** at λ = 274 nm (positive). The observation of a certain shift between the CD spectra of **1** and **2** is due to the fact that **1** und **2** are just diastereoisomers and not enantiomers. Similar behaviour was reported for *S*-[15,16] and *R*-configured[17] diolato organotitanium complexes. To confirm that the CD spectra are due to the electronic excitation of the Ti complexes, UV/Vis spectra were recorded (Figure 3, bottom). They indicate the absorption bands at the same wavelength as the corresponding CD spectra. The ligand precursors β-MeNGH_2 and α-MeNGH_2 do not demonstrate any absorption band in these regions. Therefore the CD spectra are induced by the different absolute configuration at the Ti atoms and the resulting LMCT transitions of **1** and **2**.[18]

The unexpected change of the absolute configuration at the Ti atoms is apparent furthermore by a view along the C_2 axis (Figure 4). The "S-shape" of **1** changed into an overall inverse molecular "S-shape" of **2** caused by the different coordination mode of 2,3-diolato ligands of the of the monosaccharides, which differ in configuration at the anomeric carbon atom.

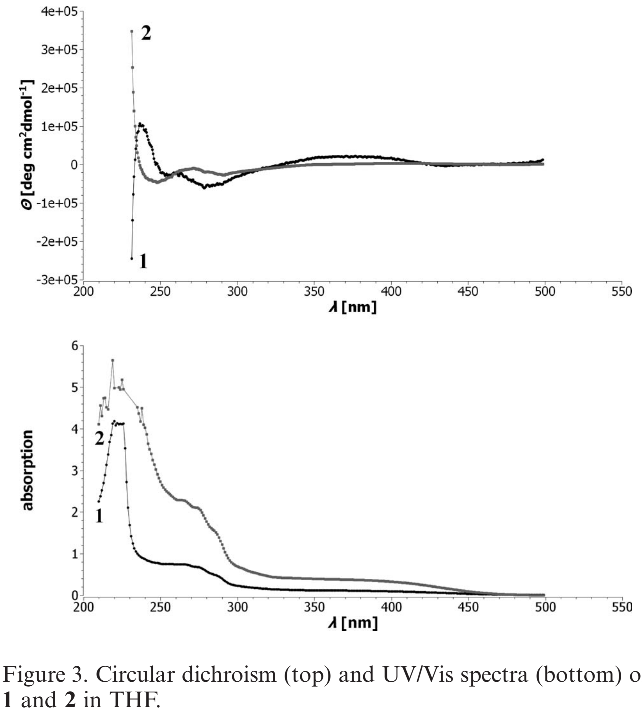

Figure 3. Circular dichroism (top) and UV/Vis spectra (bottom) of **1** and **2** in THF.

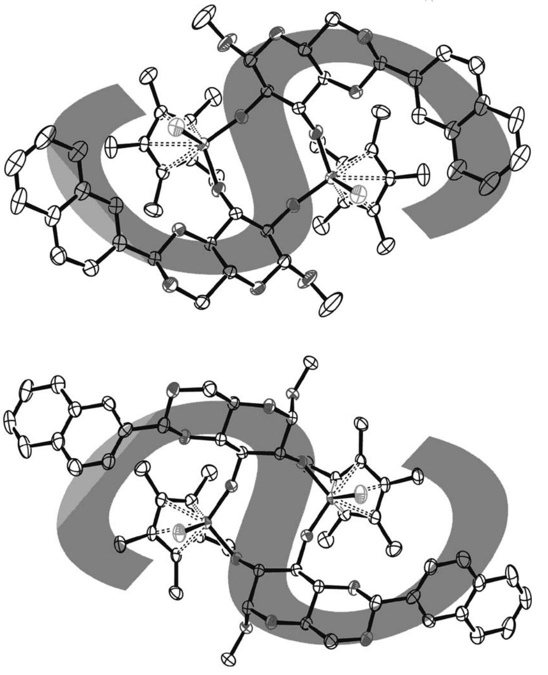

Figure 4. Overall "molecular S shape" of (a) [(Cp*TiCl)-μ-(β-MeNG)]$_2$ (**1**) and (b) [(Cp*TiCl)-μ-(α-MeNG)]$_2$ (**2**).

Conclusions

The reaction of the 1,4,6-protected α-glucopyranoside instead of the β-anomer again results in the formation of a dinuclear complex as the only isolable product. The observation of an exclusive bridging mode of the 2,3-diolato function of the monosaccharide ligand is due to the small Ti^{IV} ion.

Finally, we did not succeed in improving the coordination sphere by increasing the steric demand at the Ti atoms by using the α-anomer of the glucopyranosidato ligand instead of the β-anomer. In contrast, the formation of the dinuclear complex reflects in a change of the configuration at the Ti atoms. Besides the remarkable change in the coordination mode by the different anomers, it appears possible to assign the absolute configuration at the Ti atoms by means of ^1H NMR spectroscopy. This effect is currently investigated by using anomers of different monosaccharides. Changing configuration at the metal centres just by taking the other anomer of a monosaccharide ligand could have an important impact in metal-mediated reactions with respect to their stereoselectivity. Furthermore, we want to improve the coordination sphere of titanium atoms by derivatization of the glucopyranosidato ligands at positions 4 and 6 in a spherically more demanding way than we did in compounds **1** and **2**.

Experimental Section

All reactions were carried out with dried and distilled solvents under oxygen- and moisture-free conditions by using standard Schlenk techniques. α-MeNGH_2, β-MeNGH_2,[2,3,19,20] Cp^*TiCl_3[21,22] and **1**[4] were prepared according to literature procedures. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AVANCE 400 instrument at room temperature. *J* values are given in Hz. Elemental analysis: Vario EL III, Zentrale Elementanalytik, Department Chemie, Universität Hamburg. UV spectra were detected with a Varian Cary 5E UV/Vis/NIR Spectropolarimeter. CD Spectra were measured with a Jasco J-500C Spectropolarimeter.

Preparation of 2: α-MeNG*H*$_2$ (217 mg, 0.651 mmol) was suspended in toluene (20 mL), and NEt$_3$ (457 µL, 3.26 mmol) was added. Cp*TiCl$_3$ (189 mg, 0.651 mmol) dissolved in toluene (20 mL) was added dropwise via a dropping funnel over 20 minutes. The reaction solution was heated at reflux for 16 h and concentrated to a volume of 3 mL. *n*-Pentane (4 mL) was added to this concentrated solution, and triethylammonium chloride, which precipitated immediately, was filtered off. Compound **2** crystallizes slowly from the filtrate at room temperature in X-ray quality. After filtration, **2** was obtained as a yellow-orange solid (243 mg, 0.221 mmol, 68 %). M.p. 263 °C (decomposition). ^{1}H NMR (400 MHz, CDCl$_3$, 21 °C, TMS): δ = 1.91 (s, 15 H, Cp*), 3.41 (s, 3 H, 8-H), 3.75–3.86 (m, 3 H, 4-H, 5-H, 6-H$_{ax}$), 4.31 (dd, $^2J_{6\text{-Heq},6\text{-Hax}}$ = 10.0, $^3J_{5\text{-H},6\text{-Heq}}$ = 4.0 Hz, 1 H, 6-H$_{eq}$), 4.61 (dd, $^3J_{3\text{-H},2\text{-H};3\text{-H},4\text{-H}}$ = 8.4 Hz, 1 H, 3-H), 4.69 (d, $^3J_{1\text{-H},2\text{-H}}$ = 3.6 Hz, 1 H, 1-H), 4.73 (dd, $^3J_{2\text{-H},1\text{-H}}$ = 3.6, $^3J_{2\text{-H},3\text{-H}}$ = 8.4 Hz, 1 H, 2-H), 5.60 (s, 1 H, 7-H), 7.48–7.53 (m, 2 H, 6′-H, 7′-H), 7.70 (m≈ dd, $^3J_{3'\text{-H},4'\text{-H}}$ = 8.4, $^4J_{3'\text{-H},1'\text{-H}}$ = 1.2 Hz, 1 H, 3′-H), 7.85–7.91 (m, 3 H, 4′-H, 5′-H, 8′-H), 7.99 (m≈ s, 1 H, 1′-H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 11.9 (C-Cp*$_{prim}$), 55.4 (C-8), 62.4 (C-4), 69.5 (C-6), 81.9 (C-5), 85.2 (C-2), 85.3 (C-3), 100.0 (C-1), 102.6 (C-7), 124.6 (C-3′), 126.0 (C-7′), 126.3 (C-6′), 126.6 (C-1′), 127.7 (C-5′), 127.9 (C-4′), 128.3 (C-Cp*$_{tert}$), 128.4 (C-8′), 132.9 (C-8a′), 133.8 (C-4a′), 135.1 (C-2′) ppm. $C_{56}H_{66}Cl_2O_{12}Ti_2$ (1097.76): calcd. C 61.3, H 6.06; found C 61.4, H 6.17.

Acknowledgments

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[6] Crystal data for **2**: ($C_{56}H_{66}Cl_2O_{12}Ti_2$) at 103 K: Space group *C*2, *Z* = 2, *a* = 2334.1 (2) pm, *b* = 843.76(8) pm, *c* = 1367.19 (13) pm, $\alpha = \gamma = 90°$, β = 98.376 (2)°, *V* = 2.6639(4) nm^3, ρ = 1.369 Mg/m^3, Bruker SMART CCD diffractometer, Mo-K_α radiation, $2\theta_{max}$: 27.49°, 16042 measured data, 6022 unique data, R_{int} = 0.0483, R_1 = 0.0389, Flack parameter 0.00(2). Programs used: SAINT 6.02 [Bruker Industrial Automation, Program for data reduction, **2000**], SADABS [Program for area detector absorption corrections, Siemens Analytical X-Ray Instruments], SHELXTL-NT V 5.1 [G. Sheldrick, Bruker Crystallographic Research Systems, Bruker Analytical X-Ray Instruments Inc., Madison, Wisconsin, USA, **1997**], SHELXL-97 [G. Sheldrick, Program for crystal structure refinement, Universität Göttingen, **1997**]. Crystallographic data for the structure has been deposited with the Cambridge Crystallographic Data Centre, CCDC-741732. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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