Oxorhenium(V) Complexes of Carbohydrate Ligands[‡]

Peter Klüfers,*[a] Oswald Krotz,[a] and Martin Oßberger[a]

Keywords: Rhenium / Carbohydrates / Oxo ligands

The reaction of anhydroerythritol (AnEryt) and methyl-β-D-galactopyranoside (Me-β-D-Gal*p*) with dichloro[hydridotris(pyrazolyl)borato]oxorhenium(V) [(tpb)ReOCl$_2$] in methanol/triethylamine results in the formation of blue crystals of the diolato complexes [(tpb)ReO(AnErytH$_{-2}$)] (**1**) and [(tpb)ReO(Me-β-D-Gal*p*3,4H$_{-2}$)] (**2**). The amounts of *anti*-**1** and *syn*-**1** isomers are investigated by means of NMR spectroscopy and depend on the solvent chosen. For **2**, the generally rigid pyranoside ligand enters the complex in a conformation that is even more heavily strained than the corresponding isopropylidene sugar in terms of torsion angles. Though *anti* and *syn* isomers are also formed in non-aqueous media initially, various synthetic procedures are given to obtain pure *syn*-**2**.

Introduction

Diolato complexes of the oxo-rhenium(V) moiety have attracted considerable interest in the past decade.[1−12] Most of this work has been directed towards ethylene glycol and catechol as the ligands. Unfortunately, there is no information on rhenium complexes of diol functions incorporated into a carbohydrate. A knowledge of the rules of rhenium binding to carbohydrates is of medical significance, since it would be of great advantage to couple radioactive rhenium isotopes, which are used both in tumour diagnosis and therapy, to biomolecules that specifically bind to receptor sites of a tumour. Among the biomolecules in question, glycopeptides provide carbohydrate functionalities.

In a first attempt to learn about the structural and spectroscopic properties of rhenium-carbohydrate complexes, several furanoidic and pyranoidic diols were investigated. With this work, we report on complexes of two ligands: anhydroerythritol (AnEryt), which provides the core of *cis*-configured furanosides, and methyl-β-D-galactopyranoside (Me-β-D-Gal*p*). The latter provides diol functions, which exhibit larger torsion angles as typical for pyranosides generally.

Results and Discussion

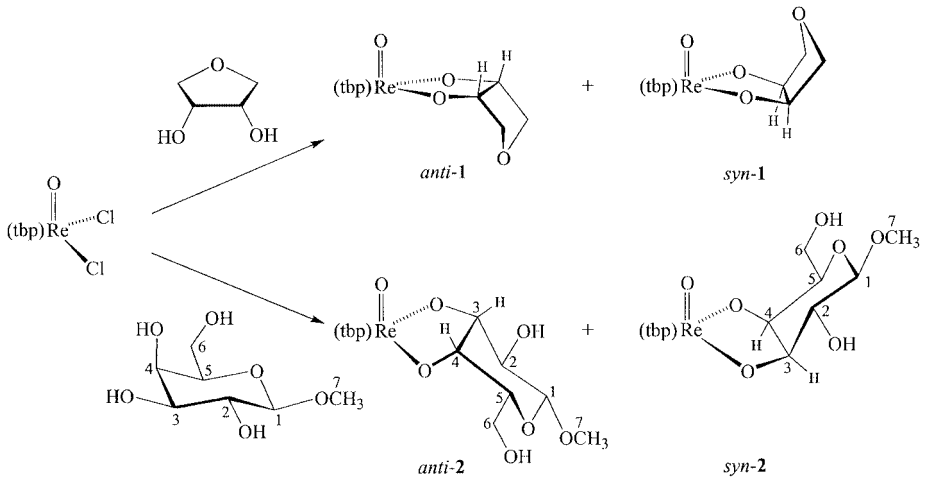
Preparation and Crystal Structures

The new compounds were prepared according to a modification of Brown and Mayer's method[7] by reaction of dichloro[hydridotris(pyrazolyl)borato]oxorhenium(V) [(tpb)ReOCl$_2$], triethylamine, and the carbohydrate in refluxing methanol (Scheme 1). To prevent formation of oligomeric rhenium complexes — obviously the main side reaction — a fourfold excess of carbohydrate over rhenium was used. Typical yields of 60% with respect to rhenium were obtained with this method. Attempts to obtain crystals were successful for both the ligands mentioned. Blue, monoclinic crystals of [(tpb)ReO(AnErytH$_{-2}$)] (**1**) are built up from equal amounts of two isomers, which differ in the orientation of the oxolanediolato ligand with respect to the (tbp)ReO fragment. Figure 1 shows the molecular structure of then *anti* isomer, highlighting an intramolecular hydrogen bond of the type C−H···O, with the ether-O atom of the ligand being the acceptor. In the *syn* isomer (Figure 2), the ligand is turned by 180° (the *syn* isomer has been defined as the one with the oxolane ring hinged towards the Re=O group). In the hydrogen-bonded *anti* form, the additional bond between the oxolanediolate and the (tpb)ReO residue results in a more perfect transfer of symmetry from the metal fragment to the ligand. Hence *anti*-**1** is close to C_s symmetry from which *syn*-**1** deviates markedly (cf. the diol torsion angles of both forms in the legends to Figure 1 and 2, the ideal angle for C_s symmetry being 0°). In the crystal structure, the ether-O atom of *syn*-**1** also acts as an acceptor in a hydrogen bond with a C−H donor; other oxygen atoms also establish weak contacts of this kind, all of which are intermolecular.

[‡] Polyol-Metal Complexes, 40. Part 39: P. Klüfers, T. Kunte, *Eur. J. Inorg. Chem.*, **2002**, 1285−1289.

[a] Department Chemie der Ludwig-Maximilians-Universität München,
Butenandtstraße 5−13, 81377 München, Germany
Fax: (internat.) + 49 (0)89/2180-7407
E-mail: kluef@cup.uni-muenchen.de

Supporting information for this article is available on the WWW under http://www.eurjic.com or from the author.



Scheme 1. Reaction scheme and numbering of carbon atoms in **2** [tpb = hydridotris(pyrazolyl)borate]

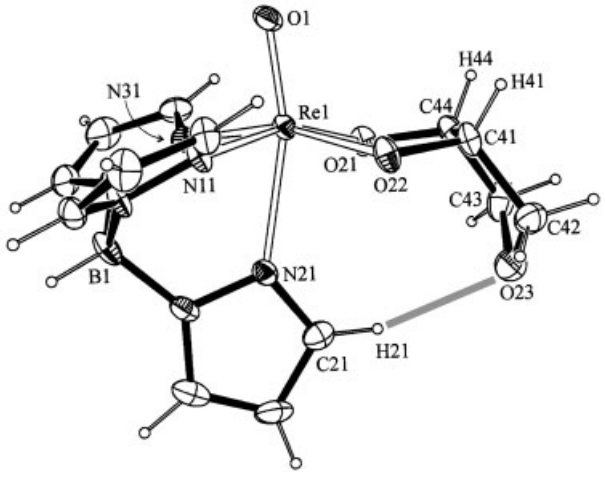


Figure 1. The structure of the H-bonded *anti* isomer of **1**; thermal ellipsoids are drawn at 40% probability; selected bond lengths (Å) and angles (°): Re1−O1 1.683(4), Re1−O21 1.929(4), Re1−O22 1.930(4), Re1−N11 2.095(4), Re1−N31 2.122(4), Re1−N21 2.291(4); O22−C41−C44−O21 −1.2(6); hydrogen bond C21−H···O23 23 3.218(7), H···O23 2.319 Å; C21−H···O23 157.8°; some of the H atoms are labelled to explain the result of an NOE experiment in the text

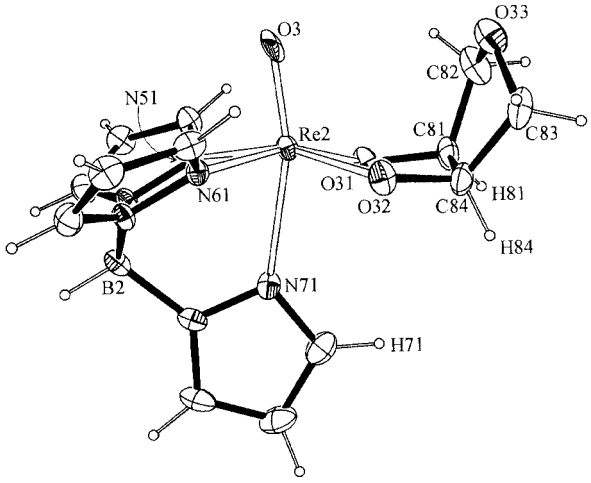


Figure 2. The structure of the *syn* isomer of **1**; thermal ellipsoids are drawn at 40% probability; selected bond lengths (Å) and angles (°): Re2−O3 1.660(4), Re2−O32 1.930(4), Re2−O31 1.932(4), Re2−N51 2.112(4), Re2−N61 2.119(4), Re2−N71 2.261(4); O31−C81−C84−O32 −19.3(6); some H atoms are labelled; in solution NMR studies, an NOE was analysed for these atoms (see text)

In a similar procedure using methyl-β-D-galactopyranoside as the polyol, blue crystals of the diolate complex [(tpb)ReO(Me-β-D-Gal*p*3,4H$_{-2}$)] (**2**) were obtained. Though the diol group with O2 and O3 is the most acidic one, a structure analysis reveals that the carbohydrate ligand binds in an O^3,O^4 bonding mode. Hence the *cis*-diol group of the pyranoside is engaged in complexation, which allows a smaller O−C−C−O torsion angle (Table 1). In **2**, the pyranose ring is found in the *syn* position (*syn* defined as in **1**). A closer inspection of the bonding parameters (Figure 3) shows the ligand to be in an unusual strained conformation. The diol torsion angles O2−C2−C3−O3 and O3−C3−C4−O4 show a 12.8° increase for the free and a 23.7° decrease for the ligating diol group with respect to the free galactoside. Hence the deviation from the unstrained conformation is much larger than would be expected from other galactopyranoside derivatives that have their O3−C3−C4−O4 fragment incorporated into a chelate ring (Table 1). For comparison, the values of the isopropylidene derivative of methyl-β-D-galactopyranoside are included in Table 1, where the differences in bond angles between metalla- (ca. 90°) and carbacycles (110−120°) are very noticeable.

The unexpectedly large distortion of the galactoside on rhenium complexation may be interpreted in terms of a mismatch between the binding sites of the metal and the diol moiety, which should result in a decreased stability of **2** with respect to **1**. In fact, **1** appears to be the product of higher stability: Batches with a 1:1 molar ratio of rhenium and galactoside hardly yielded product. On the other hand,

Table 1. Mean torsion angles τ in five-membered rings where a complex fragment L_nM (or an isopropylidene group in the last table entry) is chelated by a diolate entity derived from methyl-β-D-galactopyranoside; the torsion angles of the free galactoside are 62.9 and 56.0° for O2−C2−C3−O3 and O3−C3−C4−O4, resp.;[a] Δτ is the deviation from τ of the free galactoside; the bond length X−O (X = M or C) is given as a measure for the size of X

L_nM or Me_2C	bonding mode	X−O/Å	τ/°	Δτ/°	Ref.
(tpb)ORe^{V} (**2**)	O^3,O^4	1.944	32.3	−23.7	this work
(L-vsal)OV^{V}	O^3,O^4	2.069	44.2	−11.8	[b]
$(en)_2Co^{III}$	O^2,O^3	1.910	51.8	−11.1	[13]
isopropylidene	O^3,O^4	1.400	35.5	−20.5	[c]

[a] S. Takagi, G. A. Jeffrey, *Acta Crystallogr., Sect. B* **1978**, *34*, 2006−2010. [b] K. K. Rajak, S. P. Rath, S. Mondal, A. Chakravorty, *Inorg. Chem.* **1999**, *38*, 3283−3289; L-vsal is the salicylimide of L-valine; the galactoside ligand is the mono-anion of methyl-2,6-di-*O*-methyl-β-D-galactopyranoside, i.e. the ligand is di-*O*-methylated with respect to the other table entries. [c] P. L. Barili, G. Catelani, G. Fabrizi, D. Lamba, *Carbohydr. Res.* **1993**, *243*, 165−176.

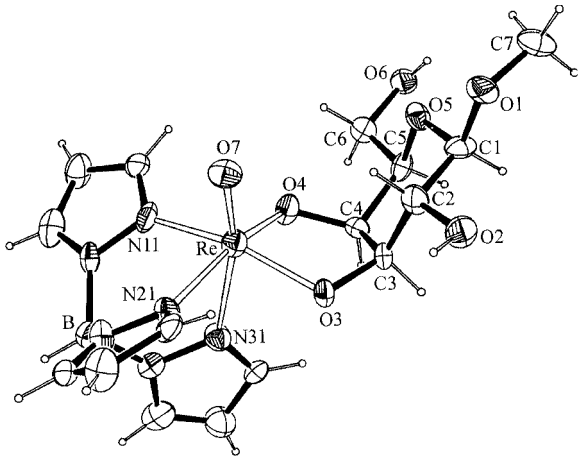


Figure 3. The molecular structure of **2**; thermal ellipsoids are drawn at 30% probability; selected bond lengths (Å) and angles (°): Re−O7 1.709(11), Re−O4 1.927(10), Re−O3 1.960(11), Re−N11 2.087(15), Re−N21 2.125(13), Re−N31 2.242(12); O3−C3−C4−O3 32.3(16), O2−C2−C3−O3 75.7(15); puckering parameters[14] of the pyranose ring: Q = 0.541(16) Å, θ = 20.3(17), φ_2 = 29(5)°

in the case of anhydroerythritol about 40% (instead of about 60% using a fourfold excess of diol) of product was obtained with the 1:1 ratio.

Solution Studies

Although *anti*-**1** and *syn*-**1** are present in equal parts in the asymmetric unit of **1**, they form in different quantities in the course of the reaction of [(tpb)$ReOCl_2$] and anhydroerythritol. After refluxing for two hours in methanol, the mixture consists of three parts of the major isomer and two parts of the minor isomer. Two sets of signals are observed in the ^1H and ^{13}C NMR spectra, and these could be assigned by means of 2D techniques as H21 and H41/H44 on one hand (Figure 1) and H71 and H81/H84 on the other (Figure 2) were well resolved. On irradiation at the frequency of the H81/H84 signal, resonance enhancement of the respective pyrazolyl-H atom (H71) was observed (the mean distance H71···H81 and H71···H84 is 3.0 Å in the crystal structure), and, likewise, irradiation at the frequency of the H71 signal resulted in resonance enhancement of the H81/H84 signal. Hence the *syn* isomer shown in Figure 2 is the minor component of the solution equilibrium. The molar ratio of the isomers depends on the solvent used. In acetonitrile, the solvent used by Brown and Mayer,[7] the *syn*/*anti* ratio increases to 4:1, whereas with water as the medium in a heterogeneous reaction, followed by dissolution of the product in dimethyl sulfoxide, a 5:1 *syn*/*anti* ratio is obtained. It should be noted, however, that due to the kinetic inertness of the complexes, these values obviously do not represent the equilibrium mixture. On prolonged heating of solutions for weeks, the isomer ratio still varies but at the same time decomposition reactions interfere with isomerization.

The ^{13}C NMR signals of both isomers were determined by a "coordination induced shift" ("CIS"), a mostly downfield shift of those carbon atoms that bear the metal-bonded oxygens. Due to the fact that rhenium(v) exhibits both a high valency and a partly filled d-shell, the CIS values are large at 28.1 ppm for *anti*-**1** and 27.1 ppm for the *syn* isomer (the methylene carbons of the oxolane ring are shifted by 3.4 and 3.0 ppm for *anti*- and *syn*-**1**, respectively).

In the case of **2**, the spectra of reaction mixtures from the methanol route consist of two signal sets, which can be assigned to *anti*-O^3,O^4- and *syn*-O^3,O^4-**2**. As with **1**, a large−although not so large−CIS is observed for C3 and C4 in the galactoside complex (Table 2). No signals have been observed that indicate O^2,O^3 isomers in solution, which are the main species in cationic complexes with the trivalent $(en)_2Co^{III}$ fragment (en = ethylenediamine).[13] An assignment of which signal set stems from the *syn* form depicted in Figure 2 was possible from NOE measurements of the same kind that have been described for **1**. These results are collected in Table 2. Despite the fact that *syn*/*anti* isomerism is also observed with **2**, all experiments support the view that no solution equilibria with significant amounts of both isomers are present for the galactoside, but instead the *syn* form is of considerably higher stability than *anti*-**2**.

Table 2. Signal positions of the methyl-β-D-galactopyranosidato(2−) ligand in ^{13}C NMR spectra of solutions of **2** in methanol; in the second and fourth numeric row Δδ, defined by $\delta_{complex} - \delta_{reference}$ is tabulated; the reference is an approximately 0.1 M solution of methyl-β-D-galactopyranoside in [D_4]methanol; Δδ values that indicate a "coordination induced shift" ("CIS") are in bold

		C1	C2	C3	C4	C5	C6	C7
syn-**2**	δ	106.0	72.4	94.8	93.0	78.0	63.7	57.5
	Δδ	−0.3	−0.4	**19.6**	**22.5**	1.1	0.9	0.0
anti-**2**	δ	105.4	71.8	94.9	91.6	78.9	62.7	57.2
	Δδ	−0.9	−1.0	**19.7**	**21.1**	2.0	−0.1	−0.3

Hence, the latter seems to be formed as an unstable intermediate only (note that *anti*-**2** is not stabilized by intramolecular hydrogen bonding). Pure *syn*-**2** is thus accessible and was obtained by several routes. Upon leaving the initial methanol solutions of both forms for about two weeks at room temperature, only *syn*-**2** is detected by NMR spectroscopy. On adding water to the reaction mixture prior to heating, only *syn*-**2** is obtained. Eventually, in a synthetic route using water as the only medium in a heterogeneous reaction, pure *syn*-**2** was also obtained. Solutions of pure *syn*-**2** in various solvents never showed formation of *anti*-**2** on heating.

Conclusion

Oxorhenium(V) complexes are kinetically inert. On reaction with a polyfunctional carbohydrate, many isomeric forms are possible in principle including isomers that are obtained by simple 180° rotation of the ligand normal to the Re=O axis (*syn*/*anti* isomers). Steric and energetic restrictions of the oxo-rhenium centre, however, reduce the number of actual species. In the case of **2**, equilibrium adjustment appears to be more rapid in aqueous media.

Experimental Section

Materials: Methyl-β-D-galactopyranoside (98%) was purchased from Fluka; anhydroerythritol was a gift from Eridania Bégin-Say; dichloro[hydridotris(pyrazolyl)borato]oxorhenium(V) was prepared according to Brown and Mayer's procedure.[7]

Spectroscopic Experiments: ^{1}H and ^{13}C NMR: Jeol EX-400. ^{1}H-^{13}C HMQC and NOE difference spectra: Jeol eclipse +500; mass spectra: Jeol JMS-700 (ionisation method: DEI$^+$). IR: Nicolet 520-FT-IR.

1: [(tpb)ReOCl$_2$] (97 mg, 0.20 mmol), anhydroerythritol (83 mg, 0.80 mmol), triethylamine (80 mg, 0.80 mmol) and 7 mL of methanol were placed in a 25 mL flask. The suspension was refluxed for 2 hours to give a dark blue solution. After cooling to room temperature, the solvent was evaporated and the residue was taken up in 3 mL of dichloromethane. The organic phase was washed

Table 3. Crystallographic data

	1	**2**
Formula	$C_{13}H_{16}BN_6O_4Re$	$C_{16}H_{22}BN_6O_7Re$
M_r/g mol^{-1}	517.322	607.400
Crystal size/mm	0.43 × 0.18 × 0.08	0.10 × 0.08 × 0.02
T/K	200(2)	200(2)
Radiation	Mo-K_α, rotating anode	Mo-K_α, rotating anode
Diffractometer	Nonius Kappa CCD	Nonius Kappa CCD
φ increment/°	1	0.3
Irradiation time/s deg^{-1}	5	80
Crystal system	monoclinic	orthorhombic
Space group	*Cc*	$P2_12_12_1$
a/Å	13.3593(2)	7.2327(8)
b/Å	8.37190(10)	14.840(2)
c/Å	29.3840(3)	19.538(3)
β/°	96.3814(5)	90
V/Å^3	3266.02(7)	2097.0(5)
Z	8	4
Calcd. density/g cm^{-3}	2.10420(5)	1.9239(5)
μ/mm^{-1}	7.474	5.846
Absorption correction	numerical (8 faces)	numerical (6 faces)
Transmission factor range	0.1651−0.5992	0.6075−0.7728
Refls. measured	13849	14707
R_{int}	0.037	0.137
Mean σ(I)/I	0.045	0.084
θ range/°	3.3−27.5	3.2−23.0
Observed refls.	6730	2290
x, y (weighting scheme)	0, 4.6734	0.0109, 22.4633
H refinement	[a]	[a]
Flack parameter	−0.017(6)	−0.02(2)
Refls. in refinement	6879	2894
Parameters	451	283
Restraints	2	0
$R(F_{obs})$	0.023	0.057
$R_w(F^2)$	0.047	0.108
S	1.045	1.115
Shift/error$_{max}$	0.001	0.001
Max. diff. density/e Å^{-3}	0.881	1.335
Min. diff. density/e Å^{-3}	−0.791	−0.747

[a] C-bonded H atoms fixed; O−H vectors were allowed to freely rotate around the C−O axis; U(H) dependent on U(pivot atom).

twice with 3 mL of water to remove triethylamine hydrochloride and unreacted anhydroerythritol, dried over magnesium sulfate and the solvents evaporated to dryness. The dark blue solid was recrystallised from toluene/*n*-pentane (ca. 1:1). Blue crystals formed within a few days at room temperature. NMR spectra of the equilibrium mixture of the two isomers of **1**: ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 3.86 (m, 2 H, H82B, H83A), 4.02 (m, 2 H, H82A, H83B), 4.21 (m, 2 H, H42A, H43B), 4.51 (d, $^2J_{H,H}$ = 11 Hz, 2 H, H42B, H43A), 5.58 (m, 2 H, H41, H44), 5.67 (m, 2 H, H81, H84), 6.05 (dd, $^3J_{H,H}$ = 2 Hz, 1 H, H22), 6.06 (dd, $^3J_{H,H}$ = 2 Hz, 1 H, H72), 6.54 (m, 4 H, H12, H32, H52, H62), 7.58 (d, $^3J_{H,H}$ = 2 Hz, 1 H, H71), 7.66 (m, 2 H, H23, H73), 7.90 (m, 4 H, H11, H31, H51, H61), 8.28 (dd, $^3J_{H,H}$ = 2 Hz, 2 H, H53, H63), 8.30 (m, 3 H, H13, H21, H33) ppm. ^{13}C NMR (100.5 MHz, [D$_6$]DMSO, 25 °C): δ = 75.0 (C82, C83), 75.4 (C42, C43), 97.9 (C81, C84), 98.8 (C41, C44), 105.6 (C72), 105.7 (C22), 108.2 (C52, C62), 108.3 (C12, C32), 134.6 (C73), 134.8 (C23), 139.4 (C13, C33, C53, C63), 142.1 (C71), 142.5 (C21), 147.7 (C51, C61), 147.9 (C11, C31) ppm. MS (70 eV): *m*/*z* (%) = 518 (100) [M$^+$], 416 (27) [M$^+$ − C$_4$H$_6$O$_3$]. IR (KBr): $\tilde{\nu}$ = 967 cm^{-1} (s; Re=O). Decomposition on heating to 218−222 °C.

2: [(tpb)ReOCl$_2$] (97 mg, 0.20 mmol), methyl-β-D-galactopyranoside (155 mg, 0.80 mmol), triethylamine (80 mg, 0.80 mmol) and 7 mL of methanol were placed in a 25 mL flask. The suspension was refluxed for 2 hours to give a dark blue solution. After cooling to room temperature the solvent was evaporated and the residue was taken up in 3 mL of dichloromethane. The organic phase was washed twice with 3 mL of water to remove triethylamine hydrochloride and unreacted galactoside. Since the aqueous phase was slightly blue, it was extracted twice with 2 mL dichloromethane. The combined organic phases were dried over magnesium sulfate and the solvent was evaporated. The dark blue solid was recrystallised from chloroform/*n*-pentane (ca. 1:1). Blue crystals formed within a few days at room temperature. The crystal that was investigated by X-ray methods was obtained by this procedure.

Solutions of pure *syn*-**2** were produced by an alternative method using water as the reaction medium: [(tpb)ReOCl$_2$] (97 mg, 0.20 mmol), methyl-β-D-galactopyranoside (155 mg, 0.80 mmol), triethylamine (80 mg, 0.80 mmol) and 7 mL of deoxygenated water were placed in a 25 mL flask. The suspension was refluxed for 3 hours, its colour turning dark blue. The resulting dark blue precipitate was filtered, extracted three times with 5 mL of acetonitrile and the organic phase evaporated to dryness. NMR spectra taken from aqueous preparations: ^{1}H NMR (400 MHz, [D$_4$]MeOH, 25 °C): δ = 3.56 (dd, 2 × $^3J_{H,H}$ = 8 Hz, 1 H, H2), 3.57 (s, 3 H. C7H$_3$), 3.91 (dd, $^3J_{H,H}$ = 7, $^2J_{H,H}$ = 11 Hz, 1 H, H62), 4.01 (dd, $^3J_{H,H}$ = 5, $^2J_{H,H}$ = 11 Hz, 1 H, H61), 4.39 (d, $^3J_{H,H}$ = 8 Hz, 1 H, H1), 4.50 (ddd, $^3J_{H5,H62}$ = 7, $^3J_{H5,H61}$ = 5, $^3J_{H5,H4}$ = 2 Hz, 1 H, H5), 4.80 (dd, $^3J_{H3,H2}$ = 8, $^3J_{H3,H4}$ = 6 Hz, 1 H, H3), 5.20 (dd, $^3J_{H4,H3}$ = 6, $^3J_{H4,H5}$ = 2 Hz, 1 H, H4), 6.03 (dd, 2 × $^3J_{H,H}$ = 2 Hz, 1 H, H32), 6.45, 6.55 (dd, 2 × $^3J_{H,H}$ = 2 Hz, 2 H, H12, H22), 7.54 (d, $^3J_{H,H}$ = 2 Hz, 1 H, H33), 7.70 (d, $^3J_{H,H}$ = 2 Hz, 1 H, H31), 7.99 (d, $^3J_{H,H}$ = 2 Hz, 1 H, H21), 8.00, 8.23 (d, $^3J_{H,H}$ = 2 Hz, 2 H, H23, H13), 8.07 (d, $^3J_{H,H}$ = 2 Hz, 1 H, H11) ppm. ^{13}C NMR (100.5 MHz, [D$_4$]MeOH, 25 °C): δ = 106.7 (C32), 109.0, 109.6 (C12, C22), 136.3 (C33), 139.6, 141.0 (C13, C23), 143.0 (C31), 149.1 (C21), 149.5 (C11) ppm; the signals of the galactoside ligand are collected in Table 2. MS (70 eV): *m*/*z* (%) = 608 (97) [M$^+$], 416 (16) [M$^+$ − C$_7$H$_{12}$O$_6$]. IR (KBr): $\tilde{\nu}$ = 970 cm^{-1} (m; Re=O). Decomposition on heating to 227−235 °C. To obtain pure *syn*-**2** in a homogeneous reaction, the methanol route was slightly altered by replacing the 7 mL quantity of methanol by a mixture of 0.8 mL of water and 6.2 mL of methanol.

X-ray Structure Determinations: Details of the structure analyses are summarized in Table 3. CCDC-179747 (**1**) and CCDC-179738 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by the Fonds der Chemischen Industrie, Frankfurt. Anhydroerythritol was gifted by Eridania Bégin-Say, Villefort, Belgium. We are indebted to Dr. P. Mayer and G. Kramer for X-ray measurements.

[1] A. Abrahams, G. Bandoli, S. Gatto, T. I. A. Gerber, J. G. H. Preez, *J. Coord. Chem.* **1998**, *43*, 297−307.
[2] D. Nunes, A. Domingos, A. Paulo, L. Patricio, I. Santos, M. F. N. N. Carvalho, A. J. L. Pombeiro, *Inorg. Chim. Acta* **1998**, *271*, 65−74.
[3] H. Sugimoto, K. Tsuge, K. Tanaka, *Chem. Lett.* **1998**, 719−720.
[4] H. Sugimoto, Y. Sasaki, *Chem. Lett.* **1997**, 541−542.
[5] P. B. Kettler, Y. D. Chang, J. Zubieta, *Inorg. Chim. Acta* **1994**, *218*, 157−165.
[6] A. Paulo, A. Domingos, A. P. Matos, I. Santos, M. F. N. N. Carvalho, A. J. L. Pombeiro, *Inorg. Chem.* **1994**, *33*, 4729−4737.
[7] S. N. Brown, J. M. Mayer, *Inorg. Chem.* **1992**, *31*, 4091−4100.
[8] J. A. Thomas, A. Davison, *Inorg. Chim. Acta* **1991**, *190*, 231−235.
[9] G. Böhm, K. Wieghardt, B. Nuber, J. Weiss, *Inorg. Chem.* **1991**, *30*, 3464−3476.
[10] J. R. Dilworth, S. K. Ibrahim, S. R. Khan, *Polyhedron* **1990**, *9*, 1323−1329.
[11] R. M. Pearlstein, A. Davison, *Polyhedron* **1988**, *7*, 1981−1989.
[12] F. Refosco, F. Tisato, U. Mazzi, *J. Chem. Soc., Dalton Trans.* **1988**, 611−615.
[13] J. Burger, P. Klüfers, *Chem. Ber.* **1995**, *128*, 75−79.
[14] D. Cremer, J. A. Pople, *J. Am. Chem. Soc.* **1975**, *97*, 1354−1358.

Received March 4, 2002
[I02107]