The First Platinum(IV) Complexes with Glucopyranoside Ligands. A New Coordination Mode of Carbohydrates

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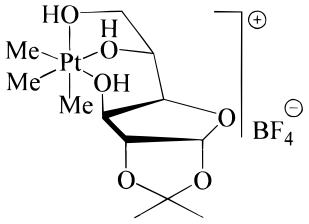
$[(PtMe_3I)_4]$ reacts with $AgBF_4$ in acetone to give *fac*-$[PtMe_3(Me_2CO)_3]BF_4$ (**2**) which was isolated as strongly moisture and air sensitive, colorless crystals and characterized by microanalysis and NMR spectroscopy (^1H, ^{13}C, ^{195}Pt). The X-ray structure analysis (orthorhombic, *Pcab*, $a = 15.599(3)$ Å, $b = 15.685(2)$ Å, $c = 15.763(3)$ Å, $Z = 8$) reveals that **2** is monomeric and that the cation exhibits local C_{3v} symmetry. The reaction of **2** with glucopyranoses (1,6-anhydro-β-D-glucopyranose (**3a**), 1-methyl-α-D-glucopyranoside (**3b**), and 1-phenyl-β-D-glucopyranoside (**3c**)) yields carbohydrate complexes $[PtMe_3L]BF_4$ (**4a**−**4c**, L = **3a**−**3c**). The complexes were characterized by microanalysis, ESI mass spectrometry and by NMR spectroscopy (^1H, ^{13}C, ^{195}Pt) displaying that the carbohydrates act as tridentate chelating ligands coordinated by the hydroxyl groups 2-OH and 4-OH and by the acetal oxygen atom of the pyranose ring. This structure was also confirmed by X-ray structure analysis of **4a** (orthorhombic, $P2_12_12_1$, $a = 6.404(1)$ Å, $b = 8.636(2)$ Å, $c = 27.161(5)$ Å, $Z = 4$). The cyclic system of the two five-membered and the one six-membered 1,3,2-dioxaplatina rings is not free from angle strain; two O−Pt−O angles are distinctly smaller than 90° (O2−Pt−O5 73.6(2), O4−Pt−O5 75.6(2)°). The Pt−O bond to the acetal oxygen atom in the pyranose ring is significantly longer (Pt−O5 2.288(5) Å) than the two Pt−OH bonds (Pt−O2 2.246(5), Pt−O4 2.248(4) and belongs to the longest Pt−O bonds at all.

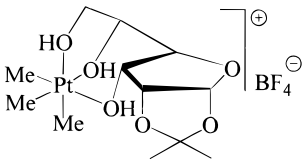
Introduction

It has been known for a long time that interactions of carbohydrates with metal ions are very important in biological processes.[1] Platinum complexes are interesting for pharmacology because of their anticancer activity.[2] Nowadays, the attention is focused on platinum(IV) complexes because of the lower toxicity of platinum(IV) and the possibility of oral administration of some potent platinum(IV) compounds in cancer chemotherapy as well as they can coordinate to the DNA without being reduced.[3,4] Thus, the coordination mode of carbohydrates to platinum(IV) might be of pharmacological interest.

Up to now, the only few known examples of carbohydrate complexes of platinum are platinum(II) complexes with functionalized carbohydrates ligated by anchor groups[5] and with nonfunctionalized carbohydrates ligated by an anionic carbon atom (carbohydrate carbanions) or by two anionic oxygen atoms (carbohydrate diolates).[6] Only very recently we were able to synthesize and characterize platinum(IV) complexes with neutral, nonfunctionalized carbohydrate ligands without anchor groups. In these complexes platinum is coordinated by three hydroxyl groups of a 1,2-*O*-isopropylidene-α-D-glucofuranose and -allofuranose ligand, respectively; see formulas **1a** and **1b**.[7]



1a



1b

We report here the first platinum(IV) complexes with neutral pyranoside ligands that are coordinated by two hydroxyl groups and the acetal oxygen atom of the pyranose ring exhibiting a new coordination mode of carbohydrates.

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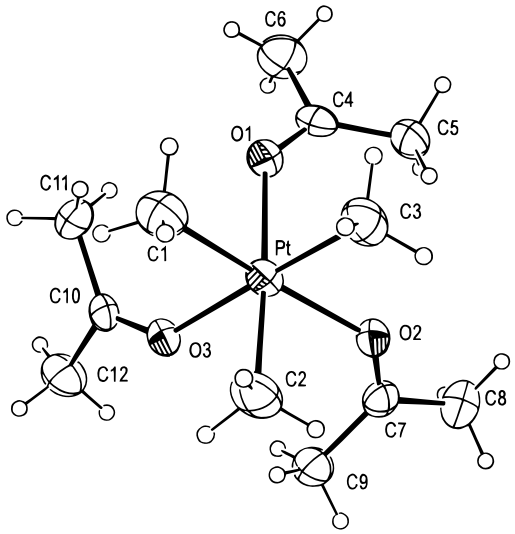


Figure 1. Molecular structure of the cation of **2**, ORTEP-III[13] diagram displaying 30% probability ellipsoids.

Table 1. Experimental Details and Crystallographic Data for Compounds **2** and **4a**

	2	**4a**
empirical formula	$C_{12}H_{27}BF_4O_3Pt$	$C_9H_{19}BF_4O_5Pt$
fw	501.24	489.14
cryst system	orthorhombic	orthorhombic
space group	*Pcab*	$P2_12_12_1$
a, Å	15.599(3)	6.404(1)
b, Å	15.685(2)	8.636(2)
c, Å	15.763(3)	27.161(5)
V, Å^3	3856(1)	1502.0(5)
Z	8	4
ρ_{calc}, g cm^{-3}	1.727	2.163
μ, mm^{-1}	7.315	9.398
θ limits, deg	2.25−24.00	2.47−25.00
no. of reflns colld	23192	8124
no. of unique reflns	3012	2638
no. of obsd reflns[a]	1986	2413
no. of data	191	181
*R*1[a]	0.0387	0.0307
*wR*2[b]	0.0691	0.0341
absolute structure parameter	−	−0.01(2)
largest peak/hole, e Å^{-3}	1.298/−0.577	1.345/−2.473

[a] $I > 2\sigma(I)$, $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] All data, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Results and Discussion

$[(PtMe_3I)_4]$[8] reacts with $AgBF_4$ in acetone to give *fac*-$[PtMe_3(Me_2CO)_3]BF_4$ (**2**), eq 1.

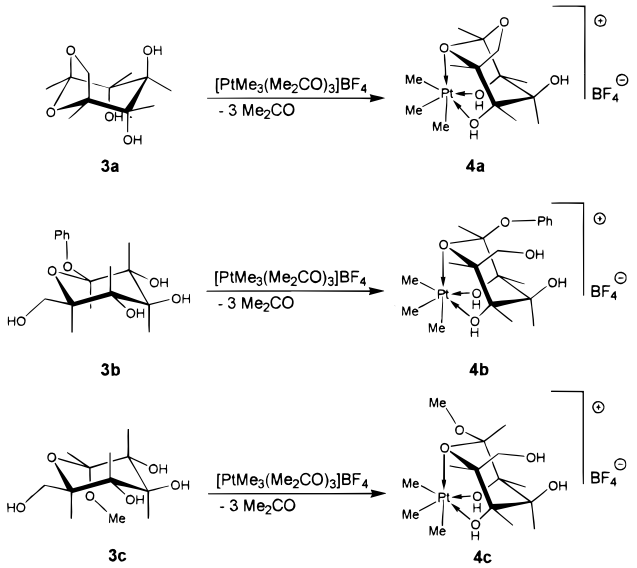
$$^1/_4[(PtMe_3I)_4] + AgBF_4 \xrightarrow{\text{acetone}} \underset{\mathbf{2}}{[PtMe_3(Me_2CO)_3]BF_4} + AgI \quad (1)$$

Complex **2** is strongly moisture and air-sensitive in solid state and is weathering at room temperature. The ^{13}C NMR spectrum reveals a downfield shift of the carbonyl group of the acetone at 12.3 ppm due to coordination (219.1 ppm in **2** vs 206.8 ppm of neat acetone). The crystal structure of **2** was determined by single-crystal X-ray crystallography (Figure 1 and Table 1). Selected bond lengths and angles are listed in Table 2. Within the tolerance limit (3σ) all three Pt−O (mean value: Pt−O 2.220 Å) and all three Pt−C bonds (mean value: Pt−C 2.02 Å) are of the same length. All angles between the same ligand in *facial* position of the coordination polyhedron are nearly orthogonal (88.1(2)−89.9(5)°). Thus, complex **2** exhibits local C_{3v} symmetry in good approximation.

Table 2. Selected Bond Lengths and Angles for **2**

Bond Lengths (Å)			
Pt−C1	2.01(1)	Pt−O1	2.214(7)
Pt−C2	2.02(1)	Pt−O2	2.236(7)
Pt−C3	2.02(1)	Pt−O3	2.211(6)
Bond Angles (deg)			
C1−Pt−C2	89.9(5)	C3−Pt−O2	89.6(4)
C1−Pt−C3	89.2(5)	C3−Pt−O3	178.8(4)
C2−Pt−C3	89.3(5)	O1−Pt−O2	89.9(4)
C1−Pt−O1	88.2(4)	O1−Pt−O3	88.1(2)
C1−Pt−O2	177.4(2)	O2−Pt−O3	89.6(2)
C1−Pt−O3	91.6(4)	O1−C4−C5	124(1)
C2−Pt−O1	177.1(4)	O1−C4−C6	118(1)
C2−Pt−O2	92.1(4)	O2−C7−C8	119.1(9)
C2−Pt−O3	89.8(4)	O2−C7−C9	123.0(9)
C3−Pt−O1	92.9(4)	O3−C10−C12	118.9(9)

Scheme 1. Synthesis of **4a**−**c**



The complexes **4a**−**c** were isolated as white air- and moisture-sensitive powders. They were fully characterized by microanalysis and by ^1H, ^{13}C, and ^{195}Pt NMR spectroscopy as well as by ESI mass spectroscopy. At room temperature, ^1H NMR spectra show a broad signal flanked by platinum satellites for the methyl protons (see Table 3). The shift (1.23−1.26 ppm) is in good accordance with the observation that stronger donor

Due to the high trans influence of the methyl ligands the Pt−O bonds are rather long revealing a weak coordination of acetone only.[9] Thus, complex **2** is a suitable starting material for substitution reactions with weak donor ligands such as carbohydrates. Complex **2** reacts with stoichiometric amounts of 1,6-anhydro-β-D-glucopyranose (**3a**), 1-methyl-α-D-glucopyranoside (**3b**), and 1-phenyl-β-D-glucopyranoside (**3c**) in acetone to give the trimethyl(carbohydrate) platinum(IV) complexes $[PtMe_3L]BF_4$ (**4a**−**4c**) (L = **3a**−**3c**) (yield: 40−81%), see Scheme 1.

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(9) For comparison *d*(Pt−O): (a) ligand L = H_2O, 202−218 pm (number of data $n = 14$); L = ROR′, 214−223 pm ($n = 9$); L = ROH, 211 pm ($n = 2$); L = RO^-, 197−215 pm ($n = 25$). Cambridge Structural Database (CSD), Cambridge Crystallographic Data Centre, University Chemical Laboratory, Cambridge (England). (b) Ligand L = $CF_3SO_3^-$, 223−232 pm ($n = 14$). Schlecht, S.; Magull, J.; Fenske, D.; Dehnicke, K. *Angew. Chem.* **1997**, *109*, 2087−2089; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1994−1995.

Table 3. Proton Chemical Shifts (in ppm) of the Methyl and the Two Coordinated Hydroxyl Groups in the Complexes **4a**−**c** (in Acetone-d_6); Coupling Constants ^2J(Pt,H) (in Hz) Are Given in Parentheses

	CH_3		OH	
	rt	−50 °C	rt[a]	−50 °C[b]
4a	1.26 (81.4)	1.03 (77.9)	8.56	6.66
		1.09 (78.7)	8.70	6.84
		1.22 (82.7)		
4b	1.23 (80.1)	1.03 (78.9)	6.40	6.69
		1.09 (78.5)	8.20	6.88
		1.22 (80.3)		
4c	1.26 (79.7)	1.03 (78.3)	6.43	6.69
		1.09 (78.3)	8.87	6.88
		1.22 (80.0)		

[a] Broad signal, low intensity. [b] Sharp signal, full intensity.

ligands L shift the signal of the methyl protons in $[PtMe_3L_3]^+$ cations to higher field (for comparison: L = Me_2CO, δ = 1.37 ppm; L = H_2O, δ = 1.06 ppm; L_3 = 1,2-*O*-isopropylidene-α-D-glucofuranose and -allofuranose, δ = 1.26 ppm).[7] At −50 °C, this broad signal is split into three signals flanked by platinum satellites revealing the nonequivalence of all three methyl groups (see Table 3). Two of which have a very similar shift at higher field (1.03−1.09 ppm), which is characteristic for methyl groups trans to hydroxyl groups. The third methyl group has a significantly lower shift (1.22 ppm) and a higher ^2J(Pt,H) coupling constant pointing to a weaker coordinating acetal oxygen in trans position.

At room temperature, two broad signals of low intensity are observed for the two coordinated hydroxyl groups. At −50 °C, two sharp singlets with the expected intensity are observed (see Table 3). Because of the insufficient solubility of the noncoordinated carbohydrates **3b** and **3c** in acetone, the difference in the chemical shifts of the hydroxyl protons in the coordinated and noncoordinated carbohydrates could be determined only in the case of **4a**/**3a**: The two hydroxyl groups (2-OH, 4-OH) bound directly to platinum are highly downfield shifted ($\Delta\delta$ = 4.8 ppm) due to coordination, whereas the noncoordinated hydroxyl group (3-OH) does not show any shift difference at complex formation.

It is apparent from the ^{1}H NMR data in acetone solution that platinum is coordinated by the hydroxyl groups 2-OH and 4-OH and by the acetal oxygen atom of the pyranose ring of the carbohydrate. It is evident from the ^{13}C NMR spectra that the complexes **4a**−**c** are isomerically pure in solution. Otherwise, the ^{13}C NMR spectroscopy is not a suitable diagnostic tool to determine the coordination mode of the carbohydrate ligands in these complexes because the carbon shift differences in the coordinated and noncoordinated ligands are small (<2 ppm).

The ^{195}Pt shift of the complexes is observed at 2315 ppm (**4a**), 2466 ppm (**4b**), and 2442 ppm (**4c**). This is a shift of 230−381 ppm to higher field compared to the tris(acetone) complex **2** ($\delta(^{195}Pt)$ = 2696 ppm). Similar values such as in the complexes **4a**−**c** were found in the trimethylplatinum(IV) furanose complexes (2350 ppm **1a**, 2520 ppm **1b**).[7]

Additionally, the existence of the compounds **4a**−**c** in acetone has been confirmed by electrospray ionization (ESI) mass spectrometry. The spectra show the expected molecular ion peaks of the $[PtMe_3(carbohydrate)]^+$ cations (*m*/*z* 402 $[PtMe_3(C_6H_{10}O_5)]^+$, **4a**; 434 $[PtMe_3(C_7H_{14}O_6)]^+$, **4b**; 496 $[PtMe_3(C_{12}H_{16}O_6)]^+$, **4c**) with the correct isotope pattern. Because the fragments are singly positive charged only, it can be deduced that no hydroxyl group of the carbohydrate ligands is deprotonated.

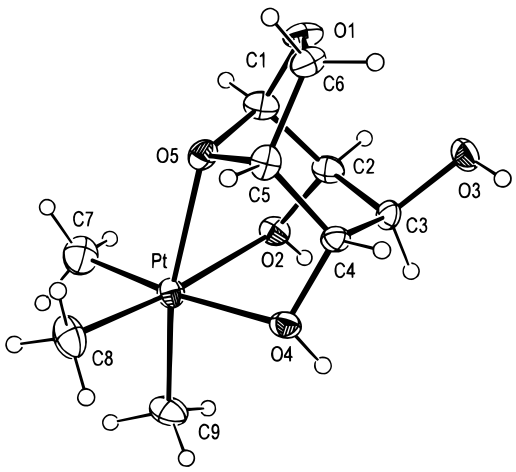

Figure 2. Molecular structure of the cation of **4a**, ORTEP-III[13] diagram displaying 30% probability ellipsoids.

Table 4. Selected Bond Lengths and Angles for **4a**

Bond Lengths (Å)			
Pt−C7	2.02(1)	O2−C2	1.445(9)
Pt−C8	2.017(8)	C2−C1	1.52(1)
Pt−C9	2.011(7)	C1−O5	1.449(9)
Pt−O2	2.246(5)	C2−C3	1.53(1)
Pt−O4	2.248(5)	C3−O3	1.439(9)
Pt−O5	2.288(4)	O5−C5	1.488(8)
Bond Angles (deg)			
C7−Pt−C8	89.9(4)	C1−O5−C5	100.4(5)
C8−Pt−C9	89.0(4)	O5−C1−C2	108.1(6)
C7−Pt−C9	88.1(4)	O3−C3−C2	107.7(6)
O2−Pt−O4	85.7(2)	O4−C4−C3	105.9(7)
O2−Pt−O5	73.6(2)	O1−C1−O5	105.3(5)
O4−Pt−O5	75.6(2)	O2−C2−C1	103.1(6)
Pt−O2−C2	110.9(4)	O5−C5−C6	101.6(6)

Recrystallization of $[PtMe_3(C_6H_{10}O_5)]BF_4$ (**4a**) from dichloromethane afforded crystals suitable for single-crystal X-ray crystallography. The molecular structure is shown in Figure 2. Selected bond lengths and angles are listed in Table 4. 1,6-Anhydro-β-D-glucopyranose acts as neutral tridentate ligand which is coordinated through two hydroxyl groups (O2, O4) and the acetal oxygen atom (O5) of the glucopyranose ring. Thus, two five-membered and one six-membered 1,3,2-dioxaplatina rings are formed exhibiting a distorted half-chair and chair conformation, respectively. The cyclic system is not free from angle strain which is revealed by the O−Pt−O angles in particular. Two of which are distinctly smaller than 90° (O2−Pt−O5, 73.6(2); O4−Pt−O5, 75.6(2)°), whereas the C−Pt−C angles remain nearly orthogonal (88.1(4)−89.9(4)°).

The two Pt−O bonds to the hydroxyl groups are equal within the tolerance limit (3σ) (Pt−O2, 2.246(5) Å; Pt−O4, 2.248(4) Å) and are equivalent to those in $[PtMe_3(C_9H_{16}O_6)]BF_4$ (**1a**) (Pt−O, 2.227(7)−2.24(1) Å). Contrarily, the Pt−O bond to the acetal oxygen is significantly longer (Pt−O5, 2.288(5) Å). This bond is one of the longest Pt−O bonds of all.[9] This may be explained in terms of the very low donor capability of the acetal oxygen atom and of the high trans influence of the methyl ligand.[10]

In the crystal all three hydroxyl groups of the carbohydrate are connected to tetrafluoroborate anions by O−H···F bridges (F2−O4″, 2.733(7) Å, F3−O2′, 2.650(7) Å, F4−O3, 2.731(8) Å) in such a way that each hydroxyl group is hydrogen-bonded

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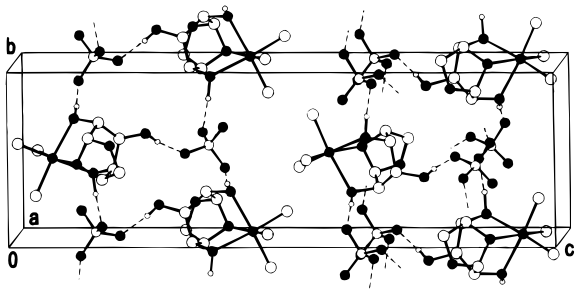

Figure 3. Cell plot of complex **4a** displaying the hydrogen bond network.

to another BF_4^- anion in the unit cell, see Figure 3. Thus, a network is formed that might be essential for the marked tendency to crystallize which is unusual for carbohydrate complexes. A similar network of O−H···F bridges is formed in the other carbohydrate platinum(IV) complex **1a**, which forms also single-crystals suitable for X-ray studies.

The new coordination mode of glucopyranose ligands by two hydroxyl groups and one acetal oxygen atom in the complexes **4a**−**c** is unique in transition metal coordination chemistry. Thus, these investigations contribute to a deeper understanding of the behavior of platinum in biological systems.

Experimental Section

Materials and General Procedures. NMR spectra were obtained on Varian Unity 500 and 2000 spectrometers using solvent signals (^{1}H,^{13}C) as internal references and $Na_2[PtCl_6]$ ($\delta(^{195}Pt) = +4520$ ppm) as an external reference, respectively. The mass spectra were performed on a ESI-mass spectrometer LCQ (Finnigan Mat) using ca. 10^{-3} M solutions of **4a**−**c** in dry acetone under the following conditions: flow 8 μL/min, ESI spray voltage 4.1 kV; capillary temperature 200 °C; sheath-gas N_2; capillary voltage 34 kV. Microanalyses were performed by the Microanalytical Laboratory of the Chemistry Department of the University. Hexachloroplatinic acid (Degussa, Saxonia) and all carbohydrates (Aldrich, Merck, Fluka) were commercial products. $[(PtMe_3I)_4]$ was prepared according to the literature.[8]

All procedures were taken under anaerobic conditions using Schlenk techniques with purified argon. The acetone was dried over B_2O_3 and distilled under argon. NMR spectra of the noncoordinated carbohydrates were recorded in acetone-d_6 (**3a**) and in methanol-d_4 (**3b**, **3c**), respectively.

Synthesis of $[PtMe_3(Me_2CO)_3]BF_4$ (2). $[(PtMe_3I)_4]$ (230 mg, 0.14 mmol) was added to a stirred solution of $AgBF_4$ (100 mg, 0.51 mmol) in acetone (20 mL) in the darkness. After 30 min AgI was removed by filtration leaving a colorless solution. The solution was concentrated to 10 mL, and diethyl ether (20 mL) was added. Cooling the solution down to −78 °C yielded strongly moisture- and air-sensitive, colorless crystals of **2** which were filtered off and dried under argon. Yield: 186 mg (68%). Found: C, 28.41; H, 5.08. Calcd for $C_{12}H_{27}BF_4O_3Pt$: C, 28.76; H, 5.43. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 1.37 (s+d, ^2J(Pt,H) = 79.5 Hz, 9H, PtCH_3), 2.09 (s, 18H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ −11.1 (s+d, ^1J(Pt,C) = 804 Hz, PtCH_3), 31.1 (s, CH_3), 219.1 (s, CO). ^{195}Pt{^{1}H} NMR (107 MHz, $(CD_3)_2CO$): δ 2696.

Synthesis of $[PtMe_3(C_6H_{10}O_5)]BF_4$ (4a). To a solution of **2** (0.51 mmol) in acetone (20 mL), prepared as described above, was added a solution of 1,6-anhydro-β-D-glucopyranose (88 mg, 0.54 mmol) in acetone (5 mL), and the resulting solution was stirred for 12 h. The solvent was then removed *in vacuo*, and the white residue was resolved in dry dichloromethane (10 mL). After 24 h the colorless crystals of **2** were filtered off and dried under argon. Yield: 142 mg (53%); mp 146 °C, decomp. above 160 °C (under argon). Found: C, 22.42; H, 4.02. Calcd for $C_9H_{19}BF_4O_5Pt$: C, 22.10; H, 3.92. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 1.26 (s+d, ^2J(Pt,H) = 81.4 Hz, 9H, PtCH_3), 4.00 (m, 4H, *H*2/*H*4/*H*6/*H*7), 4.20 (s, 1H, O*H*-3), 4.35 (s, 1H, *H*3), 4.12 (m, 1H, *H*3), 5.00 (s, 1H, *H*5), 5.80 (s, 1H, *H*1), 8.56 (s (br), O*H*-2), 8.70 (s (br), O*H*-4). ^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2CO$): δ −12.34 (s+d, ^1J(Pt,C) = 772 Hz, PtCH_3), 65.9 (*C*6), 70.2 (*C*2), 72.4 (*C*4), 73.6 (*C*3), 79.6 (*C*5), 104.8 (*C*1). ^{195}Pt{^{1}H} NMR (107 MHz): δ 2315 ($(CD_3)_2$-CO), 2609 (CD_3OD). MS, *m*/*z* (obsd/calcd): 399 (2/2), 401 (90/88), 402 (100/100), 403 (78/78), 404 (6/8), 405 (16/20), 406 (2/2).

Synthesis of $[PtMe_3(C_7H_{14}O_6)]BF_4$ (4b). Analogously to **4a**, the complex **4b** was prepared using a suspension of 1-methyl-α-D-glucopyranoside (105 mg, 0.54 mmol) in acetone (5 mL). After it had been stirred for 72 h, the clear solution was evaporated in vacuo, and the white residue was taken up in dichloromethane (10 mL). After filtration, the white powder was washed with cold diethyl ether (2 mL) and dried under argon. Yield: 112 mg (40%); mp 128 °C, decomp. above 141 °C (under argon). Found: C, 23.70; H, 4.72. Calcd for $C_{10}H_{23}BF_4O_6Pt$: C, 23.05; H, 4.45. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 1.23 (s+d, ^2J(Pt,H) = 80.1 Hz, 9H, PtCH_3), 3.37 (s, 3H, OMe), 3.55 (m, 2H, *H*3/*H*5), 3.80 (m, 4H, *H*2/*H*4/*H*6/*H*7), 4.80 (s (br), 1H, *H*1), 6.40 (s (br), 1H, O*H*-2), 8.20 (s (br), 1H, O*H*-4). ^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2CO$): δ −12.31 (s+d (br), ^1J(Pt,C) = 784 Hz, PtCH_3), 55.2 (OMe), 55.5 (*C*7), 62.7 (*C*6), 64.5(*C*4), 73.0 (*C*5), 74.3 (*C*2), 74.7 (*C*3), 100.1 (*C*1). ^{195}Pt{^{1}H} NMR (107 MHz, $(CD_3)_2CO$): δ = 2467. MS, *m*/*z* (obsd/calcd): 431 (2/2), 433 (84/87), 434 (100/100), 435 (73/79), 436 (7/9), 437 (20/20), 438 (2/2).

Synthesis of $[PtMe_3(C_{12}H_{16}O_6)]BF_4$ (4c). Analogously to **4a**, the complex **4c** was prepared using a suspension of 1-phenyl-β-D-glucopyranoside (140 mg, 0.54 mmol) in acetone (5 mL). After it had been stirred for 12 h, the clear solution was evaporated in vacuo, and the residue was resolved in dichloromethane (10 mL). After addition of hexane (5 mL) the white precipitate was filtered off, washed with diethyl ether (2 mL), and dried under argon. Yield: 260 mg (81%); mp 135 °C under decomp. (under argon). Found: C, 30.12; H, 4.08. Calcd for $C_{15}H_{25}BF_4O_6Pt$: C, 30.89; H, 4.31. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 1.26 (s+d, ^2J(Pt,H) = 80.4 Hz, 9H, PtCH_3), 3.63 (m, 4H, *H*2−5), 3.75 (m, 1H, *H*6), 3.88 (m, 1H, *H*7), 5.03 (s (br), 1H, *H*1), 7.04 (m, 3H, phenyl), 7.28 (t, 2H, phenyl). ^{13}C{^{1}H} NMR (125 MHz, $(CD_3)_2CO$): δ −12.05 (s+d (br), ^1J(Pt,C) = 798 Hz, PtCH_3), 62.6 (*C*6), 71.7 (*C*4), 74.2 (*C*2), 75.1 (*C*3), 75.9 (*C*5), 101.5 (*C*1), 117.4 (C_o), 123.2 (C_p), 130.2 (C_m), 158.5 (C_i). ^{195}Pt{^{1}H} NMR (107 MHz, $(CD_3)_2CO$): δ 2442. MS, *m*/*z* (obsd/calcd): 493 (2/2), 495 (74/83), 496 (100/100), 497 (90/81), 498 (16/14), 499 (26/20), 500 (3/3).

X-ray Crystal Structure Determinations. Colorless single crystals with platelike habit of $[PtMe_3(C_3H_6O)_3]BF_4$ (**2**) (0.20 × 0.20 × 0.05 mm) and $[PtMe_3(C_6H_{10}O_5)]BF_4$ (**4a**) (0.20 × 0.20 × 0.03 mm), respectively, were mounted on a glass fiber using perfluorinated ether and handled under a stream of cold nitrogen at 210(1) (**2**) and at 213(1) K (**4a**), respectively. Data collections were carried out on a Stoe-IPDS diffractometer with an area detector using graphite monochromatized Mo Kα radiation (λ_0 = 0.710 73 Å). The data sets were corrected numerically for absorption (T_{min}/T_{max} are 0.27/0.45 for **2** and 0.04/0.14 for **4a**, respectively (see Table 1).

The structures were solved by direct methods (SHELXS-86)[11] and refined using the full matrix least-squares method against F^2 (SHELXL-93).[12] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in calculated positions and refined with isotropic displacement parameters according to the riding model.

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Supporting Information Available: A file, in CIF format, is available on the Internet only. Access information is given on any current masthead page.

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