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SYNTHESIS AND CHARACTERIZATION OF $[PtMe_3L(H_2O)]BF_4 \cdot H_2O$ (L = 3-O-ACETYL-1,2-O-ISOPROPYLIDENE-α-D-GLUCOFURANOSE)

Reaction of $[PtMe_3(Me_2CO)_3]BF_4$ (1) with 3-O-acetyl-1,2;5,6-di-O-isopropylidene-α-D-glucofuranose in acetone affords $[PtMe_3L]BF_4$ (2) (L = 3-O-acetyl-1,2-O-isopropylidene-α-D-glucofuranose). In wet methylene chloride the complex 2 transforms to $[PtMe_3L(H_2O)]BF_4 \cdot H_2O$ (3).

Complex 3 was characterized by microanalysis and NMR spectroscopy (^1H, ^{13}C, ^{195}Pt). The X-ray structure analysis (monoclinic, $P2_1$, a = 10.529(3) Å, b = 7.322(2) Å, c = 14.668(4) Å, Z = 2) reveals that 3-O-acetyl-1,2-O-isopropylidene-α-D-glucofuranose acts as a neutral bidentate ligand which is coordinated via two hydroxyl groups ($k^2O^{5,6}$ coordination). The five-membered 1,3,2-dioxaplatina rings exhibits an envelope conformation. The coordination sphere of platinum is completed by H_2O ligand.

INTRODUCTION

The metal-binding properties of carbohydrates have been shown to be of fundamental importance in many biochemical processes such as the transport and storage of metals [1—5], the function and regulation of metalloenzymes, the mechanism of action of metal-containing pharmaceuticals, and toxic metal metabolism [6].

Platinum complexes are interesting for pharmacology because of their anticancer activity [7]. 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 [8—15]. The synthesis of these complexes is complicated by the high oxidation state of the metal ion and the reduction potential of carbohydrate.

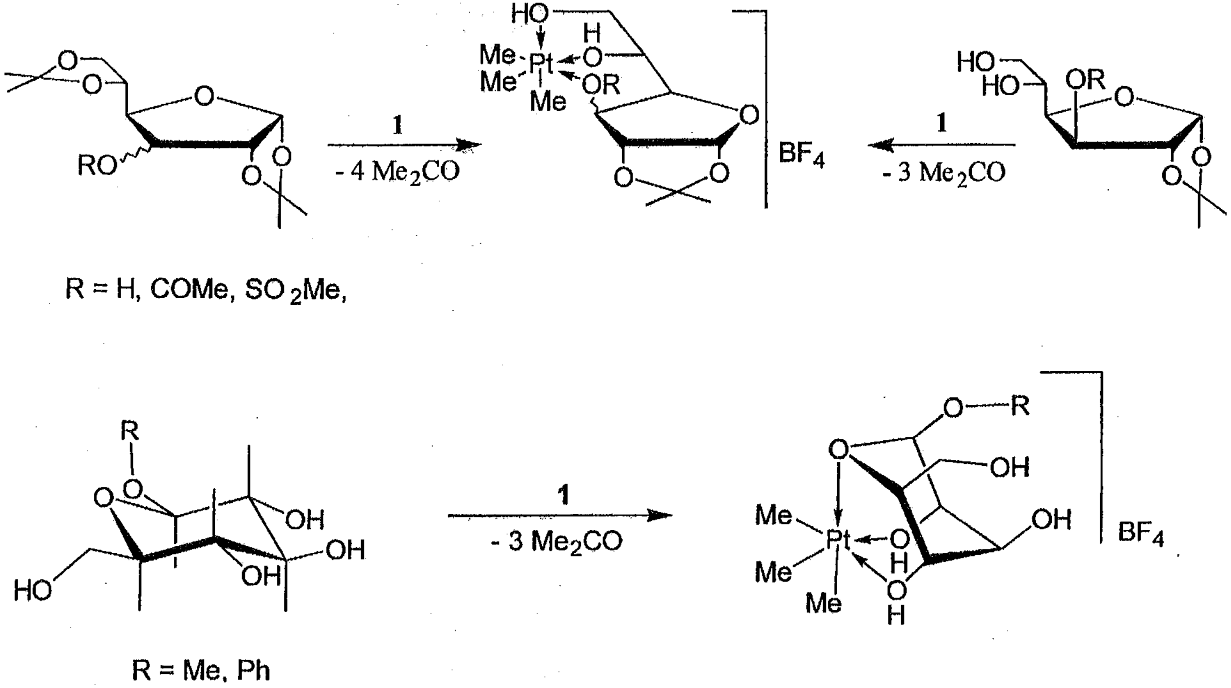
Up to now, the only few known examples of carbohydrate complexes of platinum are platinum(II) complexes with functionalized carbohydrates ligated by anchor groups [16—21] and with non-functionalized carbohydrates ligated by an anionic carbon atom (carbohydrate carbanions) [16] or by two anionic oxygen atoms (carbohydrate diolates) [22—24]. Only very recently we were able to synthesize and characterize platinum(IV) complexes with neutral, non-functionalized carbohydrate ligands without anchor groups [25—27]. This is schematically shown in Scheme 1 for the formation of platinum complexes with furanose and pyranose ligands. These reactions may be accompanied by cleavage of an isopropylidene protecting group.

Here we report on the conversion of platinum(IV) complex with a tridentately bound glucofuranose ligand [27] by water into a platinum(IV) complex in which the ligand is bidentately bound, and characterization of the obtained complex by NMR spectroscopy and X-ray analysis.

RESULTS AND DISCUSSION

$[PtMe_3(Me_2CO)_3]BF_4$ (1) reacts in acetone with 3-O-acetyl-1,2;5,6-di-O-isopropylidene-α-D-glucofuranose to give the trimethyl(carbohydrate)platinum tetrafluoroborate complex 2 in good yield (52%) (Scheme 2). In the course of the

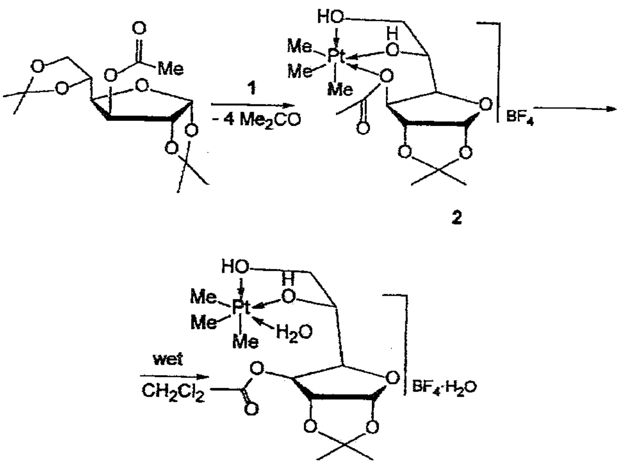
Scheme 1



R = H, COMe, SO_2Me,

R = Me, Ph

Scheme 2



2

3

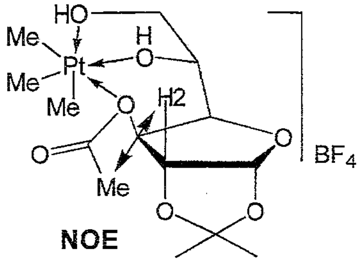
reaction the 5,6-O-isopropylidene protecting group is cleaved off and the carbohydrate ligand coordinates through the two liberated hydroxyl groups and through the ether oxygen atom of the acetoxy substituent. This coordination mode follows from NMR spectroscopical investigations (Table 1). In ^{1}H NMR spectra acquired at ambient temperature, the methyl ligands exhibit a broad signal at 1.27 ppm flanked by platinum satellites. At -50 °C, this broad signal is split into three sharp signals flanked by platinum satellites, revealing the non-equivalence of the methyl ligands. As the comparison with other complexes of the same type shows [26, 27], methyl ligands *trans* to hydroxyl groups resonate at higher field (1.03...1.10 ppm) compared to those *trans* to weaker ligands such as the ether oxygen atom of the acetoxy substituent (1.22 ppm).

Furthermore, the tridentate coordination of the carbohydrate ligand L has been established by a 2D-NOE experiment: A strong NOE was found between the methyl group of the acetoxy substituent and proton H$_{(2)}$.

Table 1

Proton chemical shifts (in ppm) of the methyl ligands and the coordinated hydroxyl groups in the complexes 2 and 3 (in d$_6$-acetone)

Complex	Coordination mode	δ (^{1}H) [^2J(Pt,H)]			δ (^{195}Pt)
		CH$_3$ (rt.)	CH$_3$ (-50 °C)	OH (-50 °C)	
2	OH, OH, OCOCH$_3$	1.25 [79.3]	1.04 [78.8] (3H)	6.65 (1H)	2624
			1.10 [78.2] (3H)	6.82 (1H)	
			1.22 [80.4] (3H)		
3	OH, OH, H$_2$O	1.20 [78.9]	1.02 [78.8] (9H)	6.65 (1H)	2360
				6.72 (5H)	



This is a strong evidence that ether oxygen atom of acetoxy substituent completes the octahedral coordination of platinum in complex **2**. The protons of hydroxyl groups coordinated to platinum atom show a broad low intensity signal at ambient temperature, whereas at −50 °C, sharp signals with the expected intensities are observed.

Complex **2** is moisture sensitive. Already in wet methylene chloride within 12 hours colorless crystals of complex **3** precipitate in good yield (64%) (Scheme 2). NMR spectroscopic investigations (Table 1) reveal that the weakest of the three oxygen donor atoms has been replaced by the stronger donating H_2O ligand.

Even at −50 °C, in ^{1}H NMR spectra the protons of all three methyl ligands are shift-equivalent by chance. This chemical shift points to three relatively strong oxygen donors in *trans* position and corresponds to similar complexes $[PtMe_3L']BF_4$ in which the carbohydrate ligand L′ is bound *via* three OH groups [25, 27]. As in complex **2**, the protons of the hydroxyl groups and the water molecules show sharp signals with the expected intensities at −50 °C only. The substitution of the weaker donating acetoxy ligand in **2** by the stronger donating water ligand in **3** results in a strong high-field shift in the ^{195}Pt resonance (2624 vs. 2360 ppm) as expected an increasing electron density at the metal center.

The structure of complex **3** was obtained by single crystal X-ray diffraction analysis. The molecular structure of the cation along with the numbering scheme is shown in Figure 1. Selected bond lengths and angles are listed in Table 2. Apart from three methyl ligands in facial position, platinum is coordinated by 3-O-acetyl-1,2-O-isopropylidene-*α*-*D*-glucofuranose and H_2O ligand. The carbohydrate acts as a neutral bidentate ligand which is coordinated via the two hydroxyl groups ($k^2O^{5,6}$ coordination). The five-membered 1,3,2-dioxaplatina rings exhibits an envelope conformation, where the atom $C_{(6)}$ is situated in

Table 2

Selected bond lengths (Å) and angles (deg.) for complex 3

$Pt—O_{(5)}$	2.239(7)	$C_{(7)}—O_{(7)}$	1.223(1)
$Pt—O_{(6)}$	2.230(7)	$C_{(7)}—O_{(3)}$	1.338(1)
$Pt—O_{(8)}$	2.197(8)	$C_{(6)}—O_{(6)}$	1.437(1)
$Pt—C_{(12)}$	2.02(2)	$C_{(5)}—C_{(6)}$	1.504(1)
$Pt—C_{(13)}$	2.00(1)	$C_{(5)}—O_{(5)}$	1.435(1)
$Pt—C_{(14)}$	2.03(1)	$C_{(3)}—C_{(4)}$	1.536(1)
$O_{(8)}—Pt—O_{(6)}$	85.2(3)	$C_{(12)}—Pt—C_{(14)}$	91.1(8)
$O_{(5)}—Pt—O_{(6)}$	75.5(3)	$C_{(5)}—O_{(5)}—Pt$	112.3(7)
$O_{(8)}—Pt—O_{(5)}$	87.8(3)	$C_{(6)}—O_{(6)}—Pt$	106.4(6)
$C_{(13)}—Pt—C_{(12)}$	90.4(8)	$C_{(2)}—C_{(3)}—C_{(4)}$	99.9(8)
$C_{(13)}—Pt—C_{(14)}$	87.6(6)	$C_{(5)}—C_{(4)}—C_{(3)}$	115.4(9)

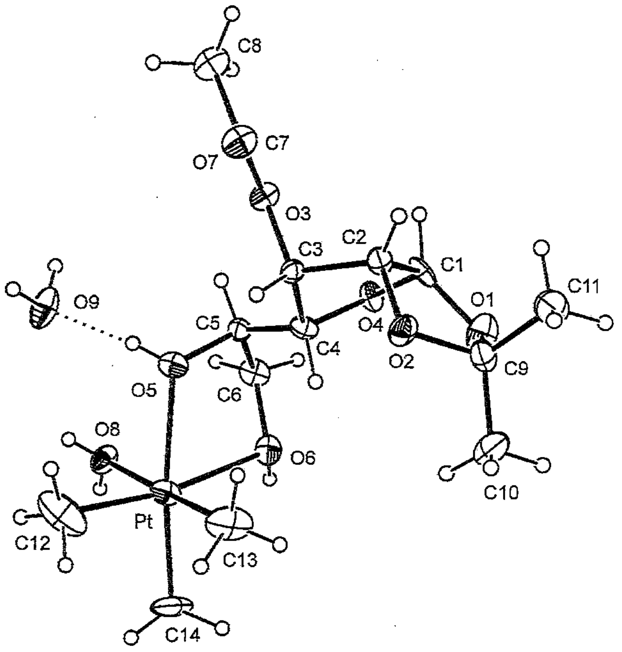


Fig. 1. Molecular structure of cation of **3** (ORTEP-III [31] diagram displaying 30% probability ellipsoids)

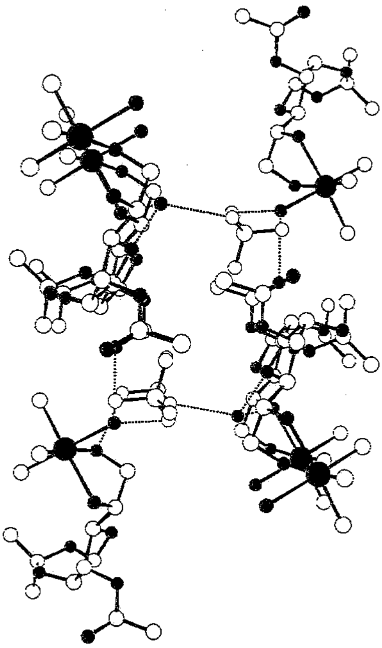


Fig. 2. Unit cell structure of the complex **3**, displaying the hydrogen bonding network

distance of 0.68(1) Å from the least-square plane formed by Pt, $O_{(5)}$, $O_{(6)}$ and $C_{(5)}$. The cyclic system is not free of bond angle strain, as indicated by O—Pt—O angles in particular. One of them is distinctly smaller than 90° ($O_{(5)}$-Pt—$O_{(6)}$ 75.5(3)°) whereas C—Pt—C angles remain nearly orthogonal (87.6(6)...91.1(8)°). The two Pt—O bonds of carbohydrate are equal within the tolerance limit (3σ) (Pt—$O_{(5)}$ 2.230(7); Pt—$O_{(6)}$ 2.239(7) Å) and are equivalent to those in $[PtMe_3L']BF_4$ (L' = 1,2-O-isopropylidene-*α*-*D*-glucofuranose) [25]. The Pt—O bond of the ligand $H_2O_{(8)}$ is significantly shorter (Pt—$O_{(8)}$ 2.197(8) Å), obviously due to the stronger donor ability of water compared with that of OH groups of carbohydrates. Interestingly, a second water molecule ($H_2O_{(9)}$) is hydrogen-bonded to the hydroxyl group $O_{(5)}$—H ($O_{(5)}$—H...$O_{(9)}$, $O_{(5)}$...$O_{(9)}$ 2.547(5) Å). Thus, the platinum carbohydrate complex tolerates at least a second equivalent of water without a complete removal of the carbohydrate ligand from the platinum(IV) center.

There are strong cation-anion interactions in 3 in the solid state via O—H...F hydrogen bonds (Figure 2). Two stronger ones are formed by hydroxyl group $O_{(6)}$—H and water molecule $H_2O_{(9)}$ ($O_{(6)}$...$F_{(1)}$ 2.717(6); $O_{(9)}$...$F_{(2)}$ 2.745(6) Å). The ligand $H_2O_{(8)}$ forms weaker hydrogen bond to fluorine atom $F_{(4)}$ ($O_{(8)}$...$F_{(4)}$ 2.979(5) Å). Furthermore, the remaining two protons of the water molecule ligand which are not involved in the O—H...F hydrogen bonds form O—H...O hydrogen bonds to the acetyl group oxygen atom of the acetoxy substituent ($O_{(8)}$...$O_{(7)}$ 2.768(6) Å) and to the acetal oxygen of the furanose ring ($O_{(9)}$...$O_{(6)}$ 2.789(7) Å), respectively. Thus, a network is built up *via* O—H...F and O—H...O hydrogen bridges in the solid state.

Complex 3 proves that a bidentatic coordination through two hydroxyl groups is sufficient to yield a stable carbohydrate platinum(IV) complex. Interestingly, this coordination is so stable that the carbohydrate ligand is not completely cleaved off by the additional water molecule present in the complex.

EXPERIMENTAL

Materials and General Procedures. NMR spectra were obtained on Varian UNITY 500 using solvent signals (^1H, ^{13}C) as internal references and $Na_2[PtCl_6]$ (δ (^{195}Pt) = +4520 ppm) as an external reference, respectively. Microanalyses were performed by the Microanalytical Laboratory in the Chemistry Department at Martin Luther University, Halle-Wittenberg. Hexachloroplatinic acid (Degussa, Saxonia) and all carbohydrates (Aldrich, Merck, Fluka) were obtained commercially, and $[(PtMe_3I)_4]$ was prepared as described previously [28].

All procedures were performed under anaerobic conditions using Schlenk techniques with purified argon. Acetone was dried over B_2O_3 and distilled under argon.

$[PtMe_3(Me_2CO)_3]BF_4$ (1). $[(PtMe_3I)_4]$ (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 dark. After 30 min, AgI was removed by filtration, leaving a colorless solution which was used without further purification.

$[PtMe_3L]BF_4$ (2) (L = 3-O-acetyl-1,2-O-isopropylidene-*α*-*D*-glucofuranose). To a solution of 1 (270 mg, 0.51 mmol) in acetone (20 ml) solution of 3-O-acetyl-1,2;5,6-di-O-isopropylidene-*α*-*D*-glucofuranose (166 mg, 0.54 mmol) in acetone (5 ml) was added under stirring. After 12 h the solvent was removed in vacuo and the white residue was redissolved in dry methylene chloride (10 ml). After addition of hexane (5 ml), the white $[PtMe_3L]BF_4$ precipitate was collected by filtration, washed with diethyl ether (2 ml), and dried under argon.

Yield: 168 mg (52%); mp 133 °C, decomp. above 142 °C (under argon). Found, %: C 28.15; H 4.25. $C_{14}H_{27}BF_4O_7Pt$. Calculated, %: C 28.53; H 4.62. ^1H NMR (500 MHz, -50 °C, $(CD_3)_2CO$) δ: 1.04/1.10/1.22 (9H, s+d, $^2J_{Pt,H}$ = 78.8/78.2/80.4 Hz, PtC$\underline{H}_3$); 6.65 (1H, s, OH); 6.82 (1H, s, OH);

^1H NMR (500 MHz, rt., $(CD_3)_2CO$) δ: 1.25 (9H, s+d (br), $^2J_{Pt,H}$ = 79.3 Hz, PtC$\underline{H}_3$); 1.26 (3H, s, CH_3); 1.43 (3H, s, CH_3); 2.04 (3H, s, CH_3CO); 3.91 (1H, dd, 5.1/8.3 Hz, $\underline{H}_{(7)}$); 4.04 (1H, dd, 5.8/8.3 Hz, $\underline{H}_{(6)}$); 4.19 (1H, dd, 2.9/7.3 Hz, $\underline{H}_{(4)}$); 4.23 (1H, ddd, 5.1/5.8/7.4 Hz, $\underline{H}_{(5)}$); 4.56 (1H, d, 3.7 Hz, $\underline{H}_{(2)}$); 5.14 (1H, d, 2.9 Hz, $\underline{H}_{(3)}$); 5.89 ppm (1H, d, 3.7 Hz, $\underline{H}_{(1)}$).

$^{13}C\{^1H\}$ NMR (100 MHz, rt., $(CD_3)_2CO$) δ: −12.1 (s+d (br), $Pt\underline{C}H_3$); 20.6 ($\underline{C}H_3CO$); 26.3 ($\underline{C}H_3$); 26.9 ($\underline{C}H_3$); 67.4 ($\underline{C}_{(6)}$); 73.4 ($\underline{C}_{(5)}$); 76.8 ($\underline{C}_{(3)}$); 83.9 ($\underline{C}_{(4)}$); 84.2 ($\underline{C}_{(2)}$); 106.2 ($\underline{C}_{(1)}$); 112.5 ($O\underline{C}O$); 170,2 ($CO_{\underline{C}H3CO}$) ppm.

$^{195}Pt\{^1H\}$ NMR (107 MHz, rt., $(CD_3)_2CO$) δ: 2624 ppm.

$[PtMe_3L(H_2O)]BF_4{\cdot}H_2O$ (3) (L = 3-O-acetyl-1,2-O-isopropylidene-*α-D*-glucofuranose). $[PtMe_3L]BF_4$ (2) (100 mg, 0.161 mmol) was redissolved in wet methylene chloride. Within 24 h, complex 3 precipitated as colorless crystals which were isolated by filtration and dried under argon.

Yield: 68 mg (64%). mp 124 °C, decomp. above 138 °C (under argon). Found, %: C 27.15; H 5.32. $C_{14}H_{31}BF_4O_9Pt$. Calculated, %: C 26.89; H 4.99. ^1H NMR (500 MHz, −50 °C, $(CD_3)_2CO$) δ: 1.02 (9H, s+d, $^2J_{Pt,H} = 78.9$ Hz, $PtC\underline{H}_3$); 6.65 (1H, s, $O\underline{H}$); 6.72 (5H, s, $O\underline{H}$, $O\underline{H}_{(2)}$); 6.94 (1H, s, $O\underline{H}$) ppm;

^1H NMR (500 MHz, rt., $(CD_3)_2CO$) δ: 1.20 (9H, s+d, $^2J_{Pt,H} = 78.7$ Hz, $PtC\underline{H}_3$); 1.27 (3H, s, $C\underline{H}_3$); 1.44 (3H, s, $C\underline{H}_3$); 2.05 (3H, s, $C\underline{H}_3CO$; 3.92 (1H, dd, $^3J_{5,7} = 4.9$, $^2J_{6,7} = 8.5$ Hz, $\underline{H}_{(7)}$); 4.04 (1H, dd, $^3J_{5,6} = 5.7$ Hz, $^2J_{6,7} = 8.5$ Hz, $\underline{H}_{(6)}$); 4.22 (2H, m, $\underline{H}_{(4)}/\underline{H}_{(5)}$); 4.56 (d, 1H, $^3J_{1,2} = 3.7$ Hz, $\underline{H}_{(2)}$); 5.15 (1H, d, $^3J_{3,4} = 2.9$ Hz, $\underline{H}_{(3)}$); 5.90 (1H, d, $^3J_{1,2} = 3.7$ Hz, $\underline{H}_{(1)}$) ppm.

$^{13}C\{^1H\}$NMR (100 MHz, rt., $(CD_3)_2CO$) δ: −12.1 (s+d (br), $Pt\underline{C}H_3$), 20.8 ($\underline{C}H_3CO$), 26.4 ($\underline{C}H_3$), 27.0 ($\underline{C}H_3$), 67.6 ($\underline{C}_{(6)}$), 73.5 ($\underline{C}_{(5)}$), 76.9 ($\underline{C}_{(3)}$), 80.6 ($\underline{C}_{(4)}$), 84.3 ($\underline{C}_{(2)}$), 106.3 ($\underline{C}_{(1)}$), 112.7 ($O\underline{C}O$), 170.4 ($CH_3\underline{C}O$) ppm.

$^{195}Pt\{^1H\}$ NMR (107 MHz, rt., $(CD_3)_2CO$) δ 2360 ppm.

X-ray Crystal Structure Determination. A suitable colorless single crystal of $[PtMe_3L(H_2O)]BF_4{\cdot}H_2O$ (3) having plate-like shape was mounted on a glass fiber using perfluorinated ether and analyzed under a stream of cold nitrogen. Intensity data were collected on a STOE IPDS diffractometer with MoKα radiation ($λ_0$ 0.71073 Å, graphite monochromator). A summary of the crystallographic data, the data collection parameters and the refinement parameters is given in Table 1. Absorption correction was carried out numerically. The structure was solved by direct methods (SHELXS-86) [29] and refined with full-matrix least-squares routines against F^2 (SHELXL-93) [30]. 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. Crystallographic data

Table 3

X-ray diffraction data for compound 3

Empirical formula	$C_{14}H_{31}BF_4O_9Pt$
Formula weight	625.29
Crystal syngony	Monoclinic
Space group	$P2_1$
Unit-cell parametrs:	
a, Å	10.529(3)
b, Å	7.322(2)
c, Å	14.668(4)
V, Å^3	1129.8(6)
Z	2
$ρ$calc, g cm^{-3}	1.838
$μ$, mm^{-1}	6.282
$θ$ range, deg	2.34...s26.03
Reflections collected	4184
Reflections obs. $[I > 2σ(I)]$	3790
No of data	298
R1[a]	0.0540
*w*R2[b]	0.1170
Absolute structure parameter	0.02(2)
Largest peak/hole, eÅ^{-3}	2.058 / −1.267

Notes:

a Obs. data, $R1 = \Sigma\,||F_o| - |F_c||\,/\,\Sigma\,|F_o|$.

b All data, $wR2 = \{\Sigma\,[w(F_o^2 - F_c^2)^2]\,/\,\Sigma\,[w(F_o^2)^2]\}^{1/2}$

(excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC-XXXX. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. Code + (1223) 336-033, e-mail: deposit@chemcrys.cam.ac.uk).

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