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Metal complexes based on monosaccharide bicyclophosphites as new available chiral coordination systems

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Abstract

1,2-*O*-Alkylidene-α-D-glucofuranose 3,5,6-bicyclophosphites form optically active complexes with simple Cu(I), Cr(0), Mo(0) and Pt(II) derivatives. All these metals are coordinated to the phosphorus atom. It was shown that copper complexes in a solution are in rapid exchange with free ligands. Depending on the reaction conditions, chromium and molybdenum can add one or two ligand molecules. *Cis–trans* isomerization is typical for the phosphite complexes of platinum in the solution. The structural parameters of some synthesised complexes were compared with those of their nearest analogues on the basis of X-ray diffraction analysis. Relatively slight deformation of ligands coordinated was inferred. Most of the metal complexes obtained are quite stable and can be used in experimental practice. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Bicyclophosphites; Metal complexes; Monosaccharides

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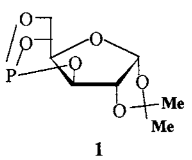
1. Introduction

Sugar derivatives whose molecules contain trivalent phosphorus groups have been coming into use for different scientific purposes, including the synthesis of metal complexes. These complexes are of interest for the development of enantioselective catalysis [1–5] and studies in a new medicobiological area [6–9]. At the same time, the search for optimal optically active ligands is far from over. Many researchers work with phosphine or phosphite derivatives of carbohydrates, which are not readily available and are readily oxidizable [10]. Non-symmetric ester phosphites and phosphonites (which are prone to disproportionation, hydrolysis and other undesirable reactions) are generally used. These ligands can present problems related to their steric individuality.

We proposed a new type of carbohydrate ligand, framework glucofuranose bicyclophosphites: 1,2-*O*-isopropylidene-α-D-glucofuranose 3,5,6-bicyclophosphite (**1**), 1,2-*O*-*R*-(2,2,2-trichlorethylidene)-α-D-glucofuranose 3,5,6-bicyclophosphite (**2**) and 1,2-*O*-isopropylidene-3-*C*-(1-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane)-α-D-glucofuranose 3,5,6-bicyclophosphite (**3**).



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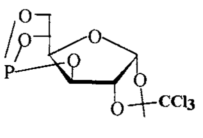

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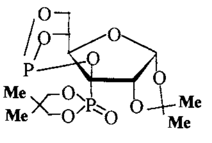

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These compounds are obtained as steric isomers and are structurally stable [11]. They are available and convenient in operation.

This article reports first on metal complexes with new

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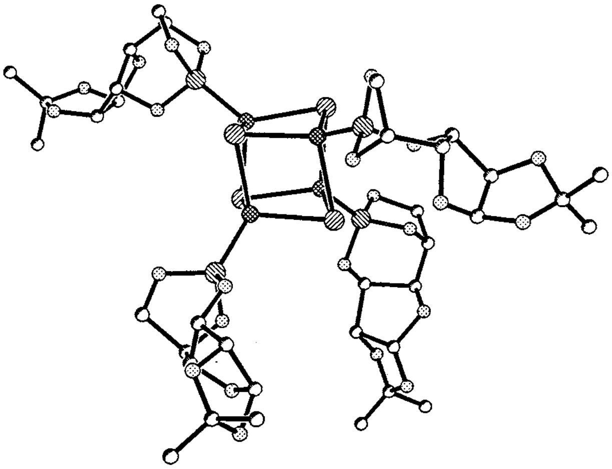


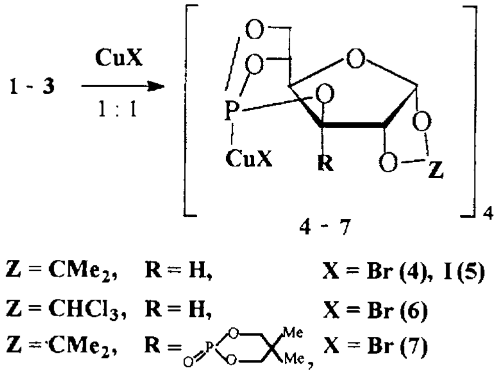
Fig. 1. Perspective drawing of the tetra-[bromo(1,2-*O*-isopropylidene-α-D-glucofuranose 3,5,6-bicyclophosphite)copper(I)] molecule.

new ligands[1] and secondly describes some chemical features of the coordination systems obtained. These features are associated with the geometry of the phosphorus atom included in the framework system of phospholane – phosphorinane ligands.

2. Results and discussion

2.1. Cu(I) complexes

We showed that ligands **1**–**3** readily react with cuprous halides in dioxane or CH_2Cl_2. The reagents taken in equimolar ratio afford individual metal complexes (**4**–**7**) in high yield.



The complexes were identified by ^{31}P-NMR spectroscopy and TLC. Their structures were supported by ^{31}P-NMR spectroscopy and X-ray diffraction analysis, with adduct **4** as an example. It has a distorted cubic structure of $L_4Cu_4Br_4$ (Fig. 1) typical for many phosphite and phosphine complexes of Cu(I) [12]. Bicyclophosphite ligands are coordinated to the tetrahedral copper and are arranged at the periphery of the molecule near cube vertexes. The Cu–Br bond length (cube edge) varies in the range 2.508–2.526 Å; the average Cu–P bond length is 2.158 Å. For phosphine metal complexes $(CuPR3X)_4$ of similar structures, these parameters are within 2.31 and 2.199 Å, respectively [13]; in the amidophosphite complex, *d*(Cu–Br) is 2.674–2.644 Å and *d*(Cu–P) is 2.174–2.179 Å [14]. The conformations of equal rings are identical for all four phosphite units in the molecule of **4**. Their structures are similar to that in free ligand **1** [11]. The main geometrical parameters of ligands in the obtained complex **4** are given in Tables 1 and 3. The ^{13}C- and ^{31}P-NMR spectral parameters of copper complexes are summarised in Table 2.

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[1] For a preliminary communication about the synthesis of some complexes from this class, see Dokl. Akad. Nauk SSSR Ser. Khim. 1997, 353(4), 508.

Table 1
Geometrical parameters of **1**, **4**, **8** and **9** from X-ray diffraction data

Compound	Cycles	Best cycle plane complanarity limits A	Cycle conformation	Deviation of atoms from the best plane, A
1	Dioxaphospholane	$PO^6C^5C^6$; 0.06	E^{O5}	0.59
4		$P^1O^{16}C^{15}C^{16}$; 0.04	E^{O15}	0.62
8		$PO^6C^5C^6$; 0.05	E^{O5}	0.63
9		$PO^6C^5C^6$; 0.05	E^{O5}	0.63
1	Dioxaphosphorinane	$PO^3C^4C^5$; 0.02	${}_{O5}C^{C3}$	−0.81; 0.51
4		$PO^{13}C^{14}C^{15}$; 0.01	${}_{O15}C^{C13}$	−0.85; 0.49
8		$PO^3C^4C^5$; 0.00	${}_{O5}C^{C3}$	−0.84; 0.49
9		$PO^3C^4C^5$; 0.02	${}_{O5}C^{C3}$	−0.85; 0.50
1	Furanose	$O^1C^1C^2C^3$; 0.15	${}^{C4}E$	0.59
4		$O^{14}C^{11}C^{12}C^{13}$; 0.07	${}^{C14}E$	0.52
8		$O^4C^1C^2C^3$; 0.04	${}^{C4}E$	0.51
9		$O^4C^1C^2C^3$; 0.04	${}^{C4}E$	0.49
1	Dioxalane	$O^4C^1C^2C^7$; 0.05	E^{O2}	0.46
4		$O^{11}C^{11}C^{12}C^{17}$; 0.03	E^{O12}	0.42
8		$O^1C^1C^2C^7$; 0.02	E^{O2}	0.41
9		$O^1C^1C^2C^7$; 0.01	E^{O2}	0.41

Table 2

^{13}C-NMR chemical shifts, δ, and $J_{^{13}\mathrm{C}-^{31}\mathrm{P}}$, Hz (in parentheses) and ^{31}P-NMR chemical shifts, δ, and $J_{^{31}\mathrm{P}-^{195}\mathrm{Pt}}$, Hz (in parentheses) compounds **4**–**9**, **12**–**14** [a]

Compound	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	P
4	106.1	84.0 (4.4)	76.1 (5.8)	77.4 (5.6)	72.7 (5.4)	68.0 (7.7)	112.5	26.8	26.3		102.7
5	105.9	83.7 (4.6)	75.6 (5.9)	77.0 (6.0)	72.2 (5.8)	67.5 (7.3)	112.5	26.4	25.9		101.6
6	105.6	84.9 (4.3)	73.9 (5.7)	77.5 (4.3)	71.2 (4.8)	66.8 (7.1)	105.4	96.1			102.5
7	106.4 (10.2)	90.5 (<1)	80.8 (114.7) (7.5)	74.9 (2.7)	81.8 (13.5)	66.4 (7.0)	115.8	28.0	27.9	33.5 (9.0)	107.6 3.4
8	106.4	84.7 (5.3)	77.2 (5.5)	78.7 (7.3)	75.1 (5.3)	69.9 (8.3)	112.6	27.0	26.4	214.8 (21.5)	186.3
9	106.5	84.6 (5.3)	77.8 (5.6)	77.8 (7.3)	74.4 (5.3)	69.3 (8.4)	113.1	27.3	26.7	203.9 (13.9)	161.6
12	105.5	83.3	78.2	80.2	75.6	69.9	112.3	26.9	26.1		87.6 (5685.6)
13	104.8	83.4	77.9	80.4	75.2	69.3	105.6	96.3			88.3 (5650.8)
14	106.8 (10.0)	90.2 (<1)	81.1 (103.9) (7.9)	78.1 (20.7)	81.3 (9.9)	67.9 (22.1)	116.3	28.1	28.0	33.6 (9.3)	85.1 1.7 (5630.2)

[a] Note: ^{13}C-NMR parameters of the cyclophosphonate unit in **7**. δ_C ppm ($J_{\mathrm{C-P}}$ Hz): C11 86.8 (7.8), C12 83.5 (8.3), C13 22.5, C14 20.5. In **14**: C11 91.6 (5.1), (5.1), C12 88.3 (5.6), (5.6), C13 22.6, C14 20.7.

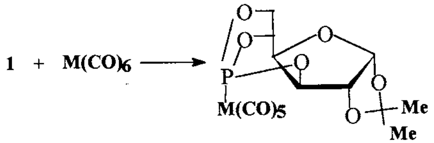
The molecular masses of adducts **4** and **6** in dioxane, determined by cryoscopy, are equal to 389 and 429; from the X-ray diffraction data, they are 1566 and 2024, respectively. Thus, the structures of copper complexes in solution and in the solid state differ significantly. The dissociation of the cube-like forms of metal complexes **4** (see Fig. 2) and **6** to monomer forms like L*CuX appears to proceed in a dilute solution. According to the literature data, similar copper complexes with simple phosphite ligands $[XCuP(OR)_3]_4$ (where R = Me, Et, ^{i}Pr, Ph) are dissociated only partly in solution. According to cryoscopic data, they have trimeric structures [15].

When studying the complexation process, we revealed the dependence of chemical shifts observed in the ^{31}P-NMR spectra of copper complexes on the ligand-to-CuX ratio. The δ_P values varied from 101 to 116 ppm. Resonance signals were shifted downfield when the amount of the ligand increased from L:CuX = 1:1 to 15:1. Only singlets have been observed. A broadening of resonance signals was observed in the ^{31}P-NMR spectra for a series of P:Cu compositions with an excess of the ligand at low temperatures (from + 20 to − 90°C). These results are evidence of exchange processes between free phosphites and their copper complexes.

No stable adducts were found in reactions with excess of the ligand. This was confirmed by the TLC data of the reaction mixtures. Spots of complex **4** and the excess ligand were observed in chromatograms. The composition with a P:Cu ratio of 1:1 also formed metal complex **4**. When an excess of CuBr was added to the reaction mixture under standard conditions, the complex with a ligand:complexing agent ratio of 1:1 was invariably formed, as shown by ^{31}P-NMR and TLC data.

2.2. Cr(0) and Mo(0) complexes

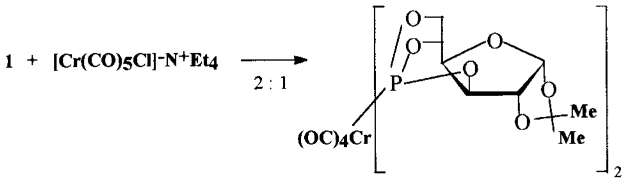
The monosaccharide phosphites under study formed complexes with chromium and molybdenum. The reaction of ligand **1** with chromium hexacarbonyl proceeded under severe conditions because of the low nucleophility of **1**. The heating of an equimolar mixture of $Cr(CO)_6$ with a ligand at 110°C for 8 h was required for obtaining complex adduct $CrL(CO)_5$. In order to accelerate the synthesis of the monodentate compound, a significant excess of complexing agent (P:Cr ca. 1:8) is advisable. Contrary to the expectations, the similar reaction between bicyclophosphite **1** and molybdenum hexacarbonyl proceeded more rapidly under milder conditions (90°C, ca. 3 h). The 20% excess of the complexing agent is most suitable for this reaction.



M = Cr (8), Mo (9)

The structures of chromium and molybdenum complexes (**8**, **9**) were supported by means of NMR and IR spectroscopy, elemental analysis and the determination of molecular mass in solution. A strong absorption and multiple lines in the 540–1450 cm^{-1} range were observed in the IR spectra of both complexes. This is associated with ν(C–O) absorption bands from the carbohydrate moiety of the ligand arisen along with ν(P–OC). The range of M–CO signals is more informative. It is known that the ν(C–O) signals of $Cr(CO)_6$ and $Mo(CO)_6$ are observed at 2000 and 2002.6 cm^{-1}, respectively. As would be expected, the IR spectra of compounds **8** and **9** exhibited three bands in a CH_2Cl_2 solution. The Cr adduct resonated at $A_1^{(2)}$ 2085 cm^{-1}, $A_1^{(1)}$ 1968 cm^{-1}, E 1952 cm^{-1}; the Mo adduct had similar ν(C–O) values equal to 2089 (w), 2070 (s) and 1955 (s), respectively. This suggested the increased electron deficiency of the glucosephosphite ligand in the compounds studied, as compared to the CO ligands in the initial hexacarbonyls. Signals from all carbon atoms of the bicyclophosphite ligand and carbonyls were observed in the ^{13}C-NMR spectra of complexes **8** and **9**. Some of signals are doublets because of the coupling constant $J_{^{13}C-^{31}P}$ (see Table 2). The molecular masses of the metal complexes determined by cryoscopy in benzene were 409 for **8** (the theoretical value being 440) and 438 for **9** (the theoretical value being 484).

The ligand exchange (religation) of $Cr(CO)_6$ and $Mo(CO)_6$ with a two-fold excess of ligand **1** was also studied. In this case, we performed the synthesis of bidentate chromium complex **10**, which required the heating of the reaction mixture at 130–140°C for 65 h. Metal complex **10** can also be obtained under mild conditions (25°C, 5 h) according to the following pathway:



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The IR spectrum of the disubstituted adduct showed a single band ν(C–O) 2047 cm^{-1}. The *trans*-$Cr(CO)_4(PR_3)_2$ complex apparently formed in this case. The molecular mass of **10** was 603 (the theoretical value is 660), the elemental analysis also supported its composition. The formation of the analogous molybdenum complex **11** was detected by means of ^{31}P-NMR spectroscopy. It was found to be a quite unstable compound, and we failed to purify it.

In order to refine the molecular structures and to evaluate the reactivity of **8** and **9**, we studied them by the X-ray diffraction method. Both complexes presented similar crystallographic parameters and molecular struc-

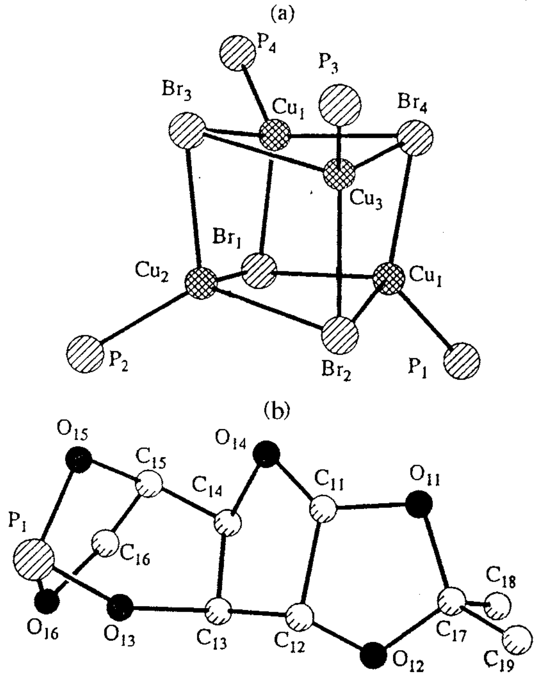

Fig. 2. (a) Cubanic fragment of the metal complex **4** molecule and (b) Biciclophosphite fragment (ligand) of the metal complex **4** molecule.

tures. Both molecules are distorted octahedrons (Figs. 3 and 4). The bicyclophosphite ligand occupies a summit. The sums of valiant angles OPO and POC are 298.3 and 336.0° in **8** and 298.9 and 336.0° in **9**, respectively. The corresponding values in the free ligand **1** are 293.2 and 340.0°, respectively [11]. Thus, the test parameters in the carbonyl complexes of Cr and Mo vary as much as in the case of copper complex **4**.

The configurations of rings in the free ligand vary only slightly during complexation. The bonds Cr–C in adduct **8** are slightly elongated as compared with those in the initial chromium hexacarbonyl (1.86–1.89 Å). The length of the Cr–CO(ax) bond is 1.888 Å, and the average Cr–CO(eq) distance is 1.896 Å. The bond Cr–P (2.245 Å) is slightly shorter than those in analogues reported $(OC)_5CrP(OR)_3$ (2.309 Å [16], 2.47 Å [17]). In molybdenum complex **9**, the bond Mo–CO(ax) is 2.017 Å and the average Mo–CO(eq) distance is 2.032 Å. These values are typical of most carbonyl complexes of Mo(0). The length of the bond Mo–P in **9** is 2.378 Å. In the phosphine analogue $(OC)_5MoPPh_3$, this parameter is equal to 2.560 Å. At the same time, there is no data in the literature on the structures of complexes with a phosphite ligand $(OC)_5MoP(OR)_3$.

2.3. Pt(II) complexes

The religation of platinum cyclooctadienyldichlorides or platinum benzonitriledechlorides by phosphites **1**–**3** proceeded readily and completely under mild conditions. According to NMR data, similar *cis*- and *trans*-bidentate complexes formed at a ratio P:Pt ca. 2:1:

$$2L + RR'PtCl_2 = L_2PtCl_2$$

$R, R' =$ 1,5-COD or $(PhCN)_2$

L = **1** (**12**), **2** (**13**), **3** (**14**)

The reaction was completed within 1 h at 20°C. The structure of metal complexes **12**–**14** was supported by the combination of elemental analysis, NMR, IR spectroscopy and cryoscopy. Along with singlets, ^{31}P-NMR spectra of all platinum adducts exhibited doublets because of the magnetic interaction between nuclei ^{31}P and ^{195}Pt. The coupling constants were more than 5500 Hz, which suggested, according to literature data [18], the *cis* arrangement of phosphite ligands in the complex molecules. Adsorption at 340 and 313 cm^{-1} was observed in the IR spectrum of the crystalline metal complex **12**. The presence of two bands also suggested the *cis*-configuration of the Pt atom $\nu(Pt–Cl_{cis})$, in contrast with $\nu(Pt–Cl_{trans})$ (single band) [19]. The ^{13}C-

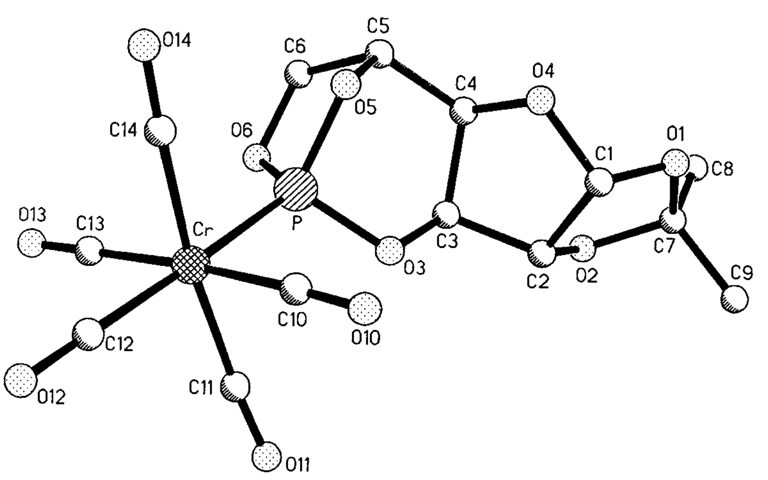

Fig. 3. Perspective drawing of the (1,2-*O*-isopropylidene-α-D-glucofuranose 3,5,6-bicyclophosphite)pentacarbonylchromium(0) molecule.

Table 3
Angles (°) and bond lengths (Å) from X-ray diffraction data

Parameter	1	[a]	[b]	[c]	4	8	9
Σ OPO	293.2	307.3	306.1	307.0	300.3	298.3	298.9
Σ POC	340.0	330.9	331.4	330.9	332.3	336.0	333.6
Σ POZ	–	347.5	348.7	349.4	353.2	354.8	354.4
d P-E	–	1.430	1.896	2.045	2.158	2.245	2.378

[a] 1,2-*O*-isopropylidene-α-D-glucofuranose 3,5,6-bicyclophosphate [20].
[b] 1,2-*O*-isopropylidene-α-D-glucofuranose 3,5,6-bicyclothiophosphate [21].
[c] 1,2-*O*-isopropylidene-α-D-glucofuranose 3,5,6-bicycloselenophosphate [21].

NMR and IR spectra of the compounds obtained exhibited no signals typical of the cyclooctadienyl and benzonitrile residues. All carbon signals observed in the spectra were typical for alkylideneglucofuranoses (nine signals for **12** and eight signals for **13**) and for the neopentyleneglycole unit (14 signals for complex **14**). Unfortunately, the signals from carbon atoms of **12** and **13** obtained in C_6D_6, CD_2Cl_2, $CDCl_3$, or $(CD_3)_2SO$ at 40°C were not split in doublets but slightly broadened. At the same time, $J_{^{13}C-^{31}P}$ cannot be equal to zero. This effect is associated with the overlapping of signals and can be explained by isomerization processes in complex molecules, i.e. by the rotation of phosphite ligands around the P–Pt bond. It should be noted that when an additional phosphorus atom has been introduced into the ligand molecule (phosphitophosphonate **3**), no similar effect was observed for metal complex **14** and most of spectral signals were doublets.

The molecular masses of complexes **12**, **13** and **14** in dioxane, determined by cryoscopy, are equal to 707, 908 and 919, respectively. They are slightly underestimated, as compared to the calculated values (762, 941 and 1058, respectively), which excludes the oligomeric structure of the metal complexes.

3. Conclusions

Thus, we have developed suitable methods for the synthesis of optically active complexes of transition metals on the basis of monosaccharide bicyclophosphites and revealed some chemical characteristics of the coordination systems obtained. We note that the framework carbohydrate ligands were not subjected to destruction in any synthesis. The availability of most compounds opens the way for their various applications.

The structural study of new complexes determined the nature of deformation of sugar ligand **1** in the process of complexation with different metals. The comparison between our results and the structural data obtained previously for bicyclophosphate derivatives [11] allowed us to trace the deforming capacity of metals as compared to that of oxygen, sulphur and selenium. The data are presented in Table 3. Metals exert a milder deforming effect on the ligand than other elements do. This results in the increased stability of metal complexes in contact with nucleophils, as compared to furanose bicyclophosphates [20,21].

4. Experimental

^{31}P-NMR spectra were recorded on a Bruker W-80 SY instrument at 32.4 MHz (with 85% H_3PO_4 as an external standard). ^{13}C-NMR spectra were recorded in integral mode with Fourier transform on a Bruker AC-200 P instrument (spectrometer frequency 50.3 MHz) relative to TMS. CD_2Cl_2 and $(CD_3)_2SO$ were used as solvents; sample concentrations were in the range 0.25–0.5 mol l^{-1}. Absorbance was measured with a DIP-360 polarimeter. X-ray analysis was performed on automatic diffractometers P3/PC Siemens (Germany) for copper adduct **4** and CAD-4 Enraf–Nonius (USA) for chromium (**8**) and molybdenum (**9**) complexes. In all cases, Mo–K_α radiation, graphite monochromator and $\theta/2\theta$ data collection were used; observed reflections: 4366(4), 1211(8), 962(9). Crystal structures were solved by direct method using SHELX (ver.5) and then refined to *R* 0.0773 (**4**), 0.0218 (**8**) and 0.0305 (**9**). Melting temperatures were determined in open capillaries on a BIT setup. Cryoscopy was performed in dry dioxane using a Beckman thermometer to determine temperature differences using water as a heat-transfer agent (0–5°C). TLC was performed with the use of Siluphol UV-254 plates and solvents: (A) benzene–dioxane (3:1); (B) benzene–dioxane (1:1); (C) hexane–dioxane (3:1); and (D) chloroform–methanol (3:1). Chromatograms were developed by the treatment with iodine vapours and calcination. All syntheses were performed in dry solvents under a dry inert gas atmosphere. 1,2-*O*-isopropylideneglucofuranose was obtained by the described procedure [22]; commercial 1,2-*O*-*R*-(2,2,2-trichlorethylidene)-α-D-glucofuranose of reagent grade was used without additional purification. Hexaethyltriamide of phosphorous acid was synthesised according to the described procedure [23]; technical trimethylphosphite was distilled from Na; chromium and molybdenum hexacarbonyls of analytical grade were used, or technical products were purified by sublimation at 140–140°C (bath) and atmospheric pressure and drying in vacuo. The synthesis of ligands **1**–**3** followed modified procedures [24–26].

4.1. *Tetra-[bromo(3,5,6-bicyclophosphite-1,2-O-isopropylidene-α-D-gluofuranose)copper(I)] (**4**)*

Freshly purified powdery CuBr (0.144 g, 1 mmol) was added to a solution of 0.248 g (1 mmol) of bicyclophosphite **1** in 8 ml of dioxane. The mixture was stirred intensively and heated for 1.5 h (60–65°C). After cooling, the solution was centrifuged and concentrated in vacuo to 2 ml; 5 ml of hexane was added. The precipitate formed was filtered off, washed with hexane and recrystallized from methylene chloride. Yield: 0.289 g (74%). M.p. 196–202°C (decomp). $[\alpha]_D$ 14.6° (*c* 1.7 DMSO). R_f 0.18 (A), 0.66 (B). Anal. Calc. for $C_{36}H_{54}Br_4Cu_4O_{24}P_4$: C, 27.59; H, 3.45; Cu, 16.22; P, 7.92; M, 1566. Found: C, 27.63; H, 3.52; Cu, 16.17; P, 7.88; M, 389.4.

4.2. *Tetra-[iodo(3,5,6-bicyclophosphite-1,2-O-isopropylidene-α-D-glucofuranose)copper(I)] (**5**)*

Analogously, 0.248 g (1 mmol) of phosphite **1** and 0.190 g (1 mmol) of CuI afforded 0.311 g of complex **5**. Yield: 74%. M.p. 240–245°C (decomp). $[\alpha]_D$ 12.2° (*c* 2.1 DMSO). R_f 0.0 (*A*), 0.51 (*B*). Anal. Calc. for $C_{36}H_{54}I_4Cu_4O_{24}P_4$: C, 24.60; H, 3.07; Cu, 14.46; I, 28.93; P, 7.06. Found: C, 24.66; H, 3.14; Cu, 14.40; I, 28.87; P, 6.98.

4.3. *Tetra-bromo(3,5,6-bicyclophosphite-1,2-O-trichlorethylidene-α-D-glucofuranose)copper(I)] (**6**)*

Analogously, 0.168 g (1 mmol) of phosphite **2** and 0.072 g (0.5 mmol) of CuBr afforded 0.162 g of complex **6**. Yield: 68%. M.p. 169–173°C (decomp). $[\alpha]_D$ 11.1° (*c* 1.6 DMSO). R_f 0.25 (*A*), 0.72 (*B*). Anal. Calc. for $C_{32}H_{32}Br_4Cl_{12}Cu_4O_{24}P_4$ (monomer in a dioxane solution): C, 19.96; H, 1.66; Cu, 13.20; P, 6.44; M, 1926. Found: C, 20.07; H, 1.71; Cu, 13.16; P, 6.39; M, 467.

4.4. *Tetra-bromo(3,5,6-bicyclophosphite-3-(1-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane)-1,2-O-isopropylidene-α-D-glucofuranose)copper(I)] (7)*

Bicyclophosphite 3 (0.0537 g, 0.22 mmol) was mixed with 0.0252 g (0.18 mmol) of CuBr in 3 ml of CH_2Cl_2 under constant stirring. The reaction lasts for 1.5 h at 20°C. The complex that had formed was precipitated from the reaction mixture by hexane and dried under water aspirator vacuum. Yield: 0.8 g (70%). M.p. 200–210°C (decomp). R_f 0.1 (A), 0.7 (B). Anal. Calc. for $C_{56}H_{88}Br_4Cu_4O_{36}P_8$: C, 30.38; H, 5.58; Cu, 18.38; P, 9.12; M, 1588. Found: C, 30.42; H, 5.61; Cu, 18.54; P, 9.03; M, 389.

Copper adducts **4**–**7** are colourless, readily soluble in CH_2Cl_2, acetone and DMSO; less soluble in dioxane, chloroform and methanol; insoluble in hexane, benzene and CCl_4.

4.5. *(3,5,6-Bicyclophosphite-1,2-O-isopropylidene-α-D-glucofuranose)pentacarbonylchrome(0) (**8**)*

4.5.1. *Method A*

Bicyclophosphite **1** (0.25 g, 1 mmol) was mixed with 1.76 g (8 mmol) of chromium hexacarbonyl, and 12 ml of toluene was added. The solution was refluxed for 3 h, cooled and filtered from the excess $Cr(CO)_6$; toluene was then evaporated in vacuo. The residue was kept at 90°C (bath) under water aspirator vacuum for 2 h and recrystallized from CH_2Cl_2. White crystals were obtained. Yield: 0.38 g (94%). M.p. 135–136 °C. R_f 0.82 (A), 0.48 (B). $[\alpha]_D$ 15.4° (*c* 2.2 DMSO). Anal. Calc. for $C_{14}H_{13}CrO_{11}P$: C, 38.18; H, 2.95; P, 7.04; M, 440. Found: C, 38.09; H, 2.89; P, 7.00; M, 418.

4.5.2. *Method B*

Phosphite 1 (0.26 g, 1.04 mmol), 0.81 g (3.68 mmol) of $Cr(CO)_6$ and 2 ml of toluene were placed into a thick-walled tube. The tube was filled with dry argon and sealed. The reaction was monitored by means of ^{31}P-NMR spectroscopy, recording spectra 0.5, 2.5, 6.5 and 8 h after beginning heating. The successive decrease of the signal at δ 117 (the initial phosphite) and the increase of the peak at δ 186 (metal complex **8**) were observed. The product was isolated analogously to method A. The yield was 0.36 g (79%); the characteristic constants of products obtained by methods A and B were identical.

4.6. *(3,5,6-Bicyclophosphite-1,2-O-isopropylidene-α-D-glucofuranose)pentacarbonylmolybdenum(0) (**9**)*

Bicyclophosphite **1** (0.25 g, 1 mmol) was mixed with 0.26 g (1 mmol) of molybdenum hexacarbonyl in 3 ml of $CH_3C_6H_5$. The reaction mixture was heated in a sealed ampoule under argon at 97–107°C (bath) for 2.5 h until the signal of the initial ligand (δ 117) in the ^{31}P-NMR spectrum disappeared totally. A light-yellow toluene solution was decanted from the minor amount of brown syrup; toluene was removed under water aspirator vacuum. The white powder that had formed was recrystallized from CH_2Cl_2 (see Fig. 4). Yield: 0.27 g (55.3%). M.p. 122°C. R_f 0.86 (A), 0.52 (B). Anal. Calc. for $C_{14}H_{13}MoO_{11}P$: C, 38.14; H, 2.91; P, 7.02; M, 484. Found: C, 38.07; H, 2.85; P, 7.02; M, 469.

4.7. *Bis(3,5,6-bicyclophosphite-1,2-O-isopropylidene-α-D-glucofuranose)pentacarbonylchromium(0)* ***(10)***

4.7.1. *Method A*

Bicyclophosphite **1** (0.25 g, 1 mmol), 0.11 g (0.5 mmol) of chromium hexacarbonyl, and 3 ml of toluene were mixed in a thick-walled tube. The tube was filled with argon and sealed. The reaction mixture was heated at 120–135°C (bath), regularly opening the tube to let CO out, until the signals at δ_P 117 (ligand) and δ_P 186 (complex **8**) in the ^{31}P-NMR spectrum disappeared totally. After heating for 67 h, only two signals at δ_P 195 and 188 with similar intensities were observed. The yellow–green solution of complex **10** was centrifuged to separate from a minor amount of black precipitate. The latter was twice washed with 2 ml of toluene; the combined toluene solution was evaporated under water aspirator vacuum and dried under a high vacuum. A white matter was obtained that was purified by recrystallization from CH_2Cl_2 or $C_2H_2Cl_2$. Yield: 0.19 g (57%). M.p. 122–123°C. R_f 0.65 (A), 0.35 (B). $[\alpha]_D$ 1.2° (*c* 1 CH_2Cl_2). Anal. Calc. for $C_{22}H_{26}CrO_{14}P_2$: C, 40.00; H, 3.94; P, 9.39; M, 660. Found: C, 41.63; H, 3.56; P, 8.81; M, 577.

4.7.2. *Method B*

A solution of 0.26 g (1.05 mmol) of bicyclophosphite **1** in 10 ml of CH_2Cl_2 was added to a solution of 0.18 g (0.50 mmol) of $(Cr(CO)_5Cl)N(C_2H_5)_2$ in 5 ml of CH_2Cl_2. The reaction mixture was stirred under argon for 5 h. The monitoring by means of ^{31}P-NMR showed that the reaction progresses by 65, 90 and 95% after 1, 2.5 and 5 h, respectively. Along with the signal from the target metal complex **10** at δ_P 188 (95%), traces of an intermediate were observed at δ_P 177 in the final ^{31}P-NMR spectrum. Methylene chloride was removed in vacuo; the greenish residue was placed into a column with SiO_2 and eluted by system A. Fractions with R_f 0.73 were collected; the solvent was removed in vacuo without heating, and the residue was dried under a high vacuum. Yield: 0.12 g (34%); syrup. R_f 0.73 (A), 0.35 (B). $[\alpha]_D$ 1.7° (*c* 1.5 benzene). Anal. Calc. for $C_{22}H_{26}CrO_{16}P_2$: C, 40.00; H, 3.94; P, 9.39; M, 660. Found: C, 41.30; H, 3.49; P, 8.73; M, 549.

4.8. *Bis(3,5,6-bicyclophosphite-1,2-O-isopropylidene-α-D-glucofuranose)tetracarbonylmolybdenum(0)* ***(11)***

Ligand **1** (0.28 g, 1.13 mmol) and $Mo(CO)_6$ (0.15 g, 0.57 mmol) were placed into an NMR spectrometer ampoule; 1 ml of toluene was added; the ampoule was filled with argon and sealed. The reaction mixture was heated at 130–160°C (bath); spectra were recorded after 3.5, 8 and 17 h. All spectra presented three signals at δ 169, 164 and 161.5 (monosubstituted complex **9**); the signal ratio 1:2:1 varied only slightly during the heating.

4.9. *Dichloro-bis(3,5,6-bicyclophosphite-1,2-O-isopropylidene-α-D-glucofuranose)platinum(II)* ***(12a)****, cis isomer*

4.9.1. *Method A*

Bicyclophosphite **1** (0.5 g, 2.00 mmol) was added to a solution of 0.38 g (1.01 mmol) of $(1.5\text{-COD})_2PtCl_2$ in 10 ml of CH_2Cl_2; the reaction mixture was stirred for 1 h, and 15 ml of hexane was added. The precipitate that had formed was filtered off and recrystallized from a CH_2Cl_2:Me_2CO (1:1) mixture. Yield: 0.48 g (62%). M.p. 238–240°C. $[\alpha]_D$ 3.6° (*c* 2.0, DMSO). R_f 0.21 (*B*), 0.74 (*D*); δ 87.8. Anal. Calc. for $C_{18}H_{26}Cl_2O_{12}P_2Pt$: C, 28.35; H, 3.41; P, 8.14; Pt, 25.59. Found: C, 28.37; H, 3.42; P, 8.11; Pt, 25.58.

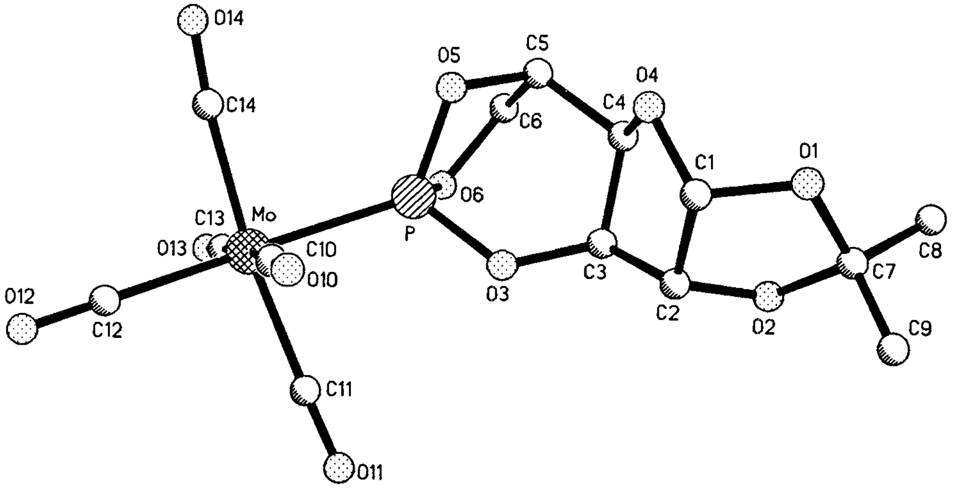

Fig. 4. Perspective drawing of the (1,2-*O*-isopropylidene-α-D-glucofuranose 3,5,6-bicyclophosphite)pentacarbonylmolybdenum(0) molecule.

4.9.2. Method B

Trans-$(PhCN)_2PtCl_2$ (0.1 g, 0.2 mmol) was added to a solution of 0.1 g (0.4 mmol) of bicyclophosphite **1** in 15 ml of CH_2Cl_2, and the reaction mixture was stirred for 45 min. The solvent was 2/3 evaporated, and 10 ml of ether was added. The crystals that had precipitated were recrystallized from an EtOH:Et_2O (1:2) mixture. Yield: 0.1 g (67%). M.p. 239–241°C. $[\alpha]_D$ 3.9° (*c* 2.4, DMSO). R_f 0.22 (B), 0.75 (D). Anal. Found: C, 25.32; H, 3.38; P, 8.10; Pt, 25.56.

*4.10. Dichloro-bis(3,5,6-bicyclophosphite-1,2-O-isopropylidene-α-D-glucofuranose)platinum(II) (**12b**), trans isomer*

Complex **12a** (0.12 g) was placed into an ampoule; 1 ml of DMSO was added, and the transformation process was monitored by means of ^{31}P-NMR spectroscopy. The initial complex exhibited a signal at δ 87.8, J_{P-Pt} 5574.8 Hz. At 25°C, the transformation began 2.5 h later and was completed after 48 h, at which time the signal of the single isomer at δ 48.1 (J_{P-Pt} 3187.9 Hz) was observed.

*4.11. Dichloro-bis(3,5,6-bicyclophosphite-1,2-O-R-(2,2,2-trichlorethylidene-α-D-glucofuranose)platinum(II) (**13**)*

4.11.1. Method A

Analogously, 0.14 g (0.2 mmol) of phosphite **2** and 0.8 g (2.14 mmol) of (1.5-COD)$_2$PtCl$_2$ gave 0.17 g of adduct **13**. Yield: 87%. M.p. 224–227°C. $[\alpha]_D$ 27.1° (*c* 3.8, DMSO). R_f 0.56 (*B*), 0.95 (*D*). Anal. Calc. for $C_{16}H_{16}Cl_8O_{12}P_2Pt$: C, 20.40; H, 1.70; P, 6.59; Pt, 20.72. Found: C, 20.36; H, 1.68; P, 6.60; Pt, 20.70.

4.11.2. Method B

Analogously, 0.34 g (0.5 mmol) of phosphite **2** and 0.23 g (0.5 mmol) of *trans*-$(PhCN)_2PtCl_2$ gave 0.36 g of adduct **13**. Yield: 75%. The characteristic constants of the compounds obtained by methods A and B were identical.

*4.12. Dichloro-bis[3,5,6-bicyclophosphite-3-(1-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane)-1,2-O-isopropylidene-α-D-glucofuranose)platinum(0) (**14**).*

Ligand **3** (0.086 g, 0.22 mmol) in 2 ml of CH_2Cl_2 was treated with 0.0406 g (0.11 mmol) of CODPtCl$_2$ in 2 ml of CH_2Cl_2. After stirring for 1.5 h, the solvent was 2/3 removed in vacuo, and the reaction product was precipitated by hexane. Yield: 0.099 g (86%). M.p. 235–237°C. $[\alpha]_D$ 27.3° (*c* 1.0, CH_2Cl_2). R_f 0.47 (A), 0.53 (B). Anal. Calc. for $C_{28}H_{44}Cl_2O_{18}P_4Pt$: C, 21.76; H, 2.11; P, 6.87; Pt, 20.86; M, 1058. Found: C, 21.69; H, 2.09; P, 6.78; Pt, 20.92; M, 989. Compounds **12a – 14** are colourless, soluble in $CHCl_3$, CH_2Cl_2, dioxane and acetone; less soluble in benzene and ether; insoluble in hexane and water.

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