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Chelate-stabilized alkoxopalladium(II) complexes with chiral phosphine-substituted carbohydrate ligands†

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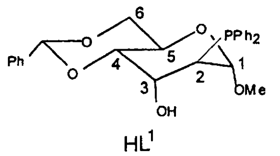
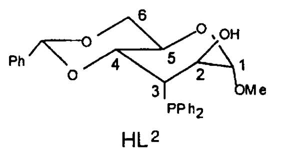
The reactions of chiral P,O-bidentate methyl 4,6-*O*-benzylidene-2-deoxy-2-(diphenylphosphino)-α-D-altropyranoside (HL^1) and methyl 4,6-*O*-benzylidene-3-deoxy-3-(diphenylphosphino)-α-D-altropyranoside (HL^2) with [PdCl$_2$(cod)] (cod = cycloocta-1,5-diene) or [PdCl$_2$(NCMe)$_2$] gave the complexes *trans*-[PdCl$_2$(HL)$_2$] (L = L^1 **1a** or L^2 **1b**). Complex **1b** crystallizes in the tetragonal space group $P4_12_12$, with a = 12.326(2), c = 32.649(8) Å and Z = 4, R = 0.023 for 2502 reflections having $I \geqslant 3\sigma(I)$. The large deviation (14.6°) of the angle P–Pd–P′ from 180° may be ascribed to the overcrowding of the bulky phosphine ligands. Treatments of **1a** and **1b** with NaOMe in methanol gave the corresponding bis(alkoxo) complexes *cis*-[PdL$_2$] **2a** and **2b**. The compounds have been characterized by infrared, Raman, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. The Pd–O absorption appears at 388 cm^{-1} for **2a** and 366 cm^{-1} for **2b**. The *cis* and *trans* geometries have been assigned by Raman spectroscopic studies.

Functional phosphines containing oxygen donor atoms are of considerable interest,[1] in particular with respect to the development of novel homogeneous catalysts. As P,O chelating ligands they exhibit unusually enhanced selectivity in nickel-catalysed oligomerization and polymerization of ethene[2] and in the carbonylation and hydrocarbonylation of methanol to oxygen-containing C$_2$ products.[3–6] Moreover, they have also been used in stereoselective hydrogenation,[7] hydrosilylation[8] and hydroformylation.[9] In some cases, alkoxopalladium complexes are postulated to be intermediates in the stoichiometric or catalytic reactions of palladium complexes in alcoholic solvents.[10,11] However, the chemistry of such complexes has not yet been explored[12,13] much because isolable complexes are rare and often unstable due to the formation of hydrides or the precipitation of palladium(0).

We have found an effective method[14] to incorporate phosphorus atoms into the pyranose ring and have prepared two optically active phosphines, methyl 4,6-*O*-benzylidene-2-deoxy-2-(diphenylphosphino)-α-D-altropyranoside (HL^1) and methyl 4,6-*O*-benzylidene-3-deoxy-3-(diphenylphosphino)-α-D-altropyranoside (HL^2) which possess both ether- and hydroxy-oxygen donors. In this paper we report the syntheses and structural characterization of some of their palladium(II) complexes, including two alkoxo- complexes.



HL^1



HL^2

Experimental

The compounds[14] HL^1 and HL^2, [PdCl$_2$(cod)][15] (cod = cycloocta-1,5-diene) and [PdCl$_2$(NCMe)$_2$][16] were prepared by literature methods. The NMR spectra were recorded on a Varian Unity-500 spectrometer operating at 499.98 MHz for ^{1}H, 125.71 MHz for ^{13}C and 202.36 MHz for ^{31}P. Chemical shift data are in ppm, referred to internal SiMe$_4$ for ^{1}H and ^{13}C and to external 85% H$_3$PO$_4$ for ^{31}P. Two-dimensional correlation (COSY) and heteronuclear multiple-quantum coherence (HMQC) NMR spectra were measured using standard techniques. Infrared spectra were measured on a Nicolet Magna-750 FT-IR (in KBr discs, 4000–400 cm^{-1}) or a Digilab FTS-20 E/D-V spectrometer (in Nujol, 550–80 cm^{-1}), resonance Raman spectra on a Nicolet 910 FT-Raman spectrometer using a Raman 1064 nm laser source at a resolution of 2 cm^{-1} with 200–400 scans. Elemental analyses were performed by the analytical laboratory of this Institute.

Preparations

[PdCl$_2$(HL^1)$_2$] 1a and [PdCl$_2$(HL^2)$_2$] 1b. A solution of HL^1 or HL^2 (0.90 g, 0.2 mmol) in dichloromethane (5 cm^3) was added to a solution of [PdCl$_2$(cod)] or [PdCl$_2$(NCMe)$_2$] (0.1 mmol) in dichloromethane (5 cm^3) to give a yellow-orange solution. This was stirred for 0.5 h at room temperature, and then concentrated to *ca.* 1 cm^3. Hexane was added to afford a yellow precipitate of complex **1a** and an orange one of **1b**.

[PdL$_2$] (L = L^1 2a or L^2 2b). A mixture of complex **1a** or **1b** (0.1 g, 0.1 mmol) and NaOMe (0.1 g, 2 mmol) was stirred in methanol (2 cm^3) at room temperature for 1 h. The tan product (**2a** or **2b**) was obtained by filtration after adding water (5 cm^3) to the solution.

Crystallography

Suitable crystals of complex **1b** were obtained by slow evaporation of a dichloromethane–hexane solution. A single crystal with dimensions 0.20 × 0.40 × 0.40 mm was mounted on a glass fibre in a random orientation. X-Ray diffraction measurements were performed at 296 ± 1 K on an Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo-Kα radiation.

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† Chiral Phosphine Ligands derived from Sugars. Part 5.

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Crystal data. $C_{52}H_{54}Cl_2O_{10}P_2Pd$, M = 1078.26, tetragonal, space group $P4_12_12$ (ITC no. 92), a = 12.326(2), c = 32.649(8) Å, U = 4960.1 Å^3, D_c = 1.44 g cm^{-3}, Z = 4, F(000) = 2224, μ(Mo-Kα) = 6.0 cm^{-1}, λ(Mo-Kα) = 0.710 73 Å.

The cell parameters were obtained by least-squares fit of 25 reflections in the range 14 < θ < 15. A total of 5444 reflections were collected by variable-speed ω–2θ scan up to 52°. Three standard reflections were used to check the stability of the crystal and of the experimental conditions and were measured every hour, but no significant variation was detected. Data were corrected for Lorentz-polarization factors using the data-reduction programs of the MOLEN[17] crystallographic program package. From 2903 unique reflections, 2502 were considered observed [$I \geqslant 3\sigma(I)$] for the refinement of the structure.

The structure was solved by direct methods. Three atoms were located from an E-map prepared and the remaining non-hydrogen atoms were located in successive difference Fourier syntheses. Hydrogen atoms were located from the difference Fourier map and their positions and isotropic thermal parameters were refined. The structure was refined by full-matrix least squares minimizing the function $\Sigma w(F_o - F_c)^2$ and converging to $R = \Sigma|F_o - F_c|/\Sigma F_o = 0.023$ and $R' = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{\frac{1}{2}} = 0.026$ with the final weighting scheme $w = 1/[\sigma(F^2) + (0.020F)^2 + 1]$. The largest parameter shift in the final cycle of refinement $(\Delta/\sigma)_{max}$ was 0.10. The maximum and minimum heights in the final Fourier difference map were 0.30 and −0.07 e Å, respectively.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/95.

Results and Discussion

Syntheses and spectroscopic studies

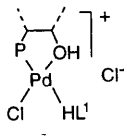
The compounds HL^1 and HL^2 react with $[PdCl_2(cod)]$ in dichloromethane to give stoichiometric amounts of complexes $[PdCl_2(HL)_2]$ (L = L^1 **1a** or L^2 **1b**) (Scheme 1). Elemental analysis and some physical data are listed in Table 1. The Pd–Cl absorptions[13,18–20] at 365 cm^{-1} for **1a** and 349 cm^{-1} for **1b** indicate that both complexes are of *trans* geometry. However, the sharp peaks in the $^{31}P\text{-}\{^1H\}$ NMR spectra of **1a** (δ 21.4) and **1b** (δ 21.9) in $CDCl_3$ are similar to those of the *cis* isomer of $[PdCl_2L_2]$ [L = $Ph_2PCH_2C(O)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$].[21] In order to clarify the configurations, reactions of HL^1 and HL^2 with $[PdCl_2(NCMe)_2]$ in dichloromethane were carried out, giving the complexes $[PdCl_2(HL)_2]$ with the same $^{31}P\text{-}\{^1H\}$ NMR and IR spectra as those of **1a** and **1b**, indicating that they indeed have the *trans* geometries both in the solid state and in $CHCl_3$, as *trans* products were often reported[13] for reactions with $[PdCl_2(NCMe)_2]$.

$$[PdCl_2L'] \xrightarrow{(i)} \underset{\textbf{1a, 1b}}{trans\text{-}[PdCl_2(HL)_2]} \xrightarrow{(ii)} \underset{\textbf{2a, 2b}}{cis\text{-}[PdL_2]}$$

Scheme 1 (*i*) L′ = cod or $(NCMe)_2$, HL^1 or HL^2 in CH_2Cl_2; (*ii*) NaOMe in MeOH

Proton NMR measurements revealed that compounds **1a** and **1b** are not stable in $CDCl_3$, particularly the former. A CHO proton signal at δ 10.0 suggests the presence of free PhCHO in $CDCl_3$, as was also observed for $[AuCl(HL^1)]$.[22] This means that an alcohol–palladium(II) species exists even in $CDCl_3$, although this was not detected by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. The alcohol–palladium(II) complexes form easily in MeOH and could be isolated with the aid of $AgClO_4$.[13] On dissolving compound **1a** in $CDCl_3$ and as soon as a trace of the alcohol–palladium(II) species **3** is formed, the dissociated HCl immediately causes hydrolysis of the molecule to give PhCHO. Satisfactory one- and two-dimensional NMR spectra can be afforded by using a fresh sample for every measurement to avoid hydrolysis.

Chemical shifts of the complexes are listed in Tables 2 and 3 for ^1H and ^{31}P and ^{13}C, respectively, accompanied by the values of free HL^1 and HL^2 for comparison. The ^1H NMR spectra cannot be analysed simply, mainly owing to long-range virtual coupling,[23,24] and some coupling constants are not



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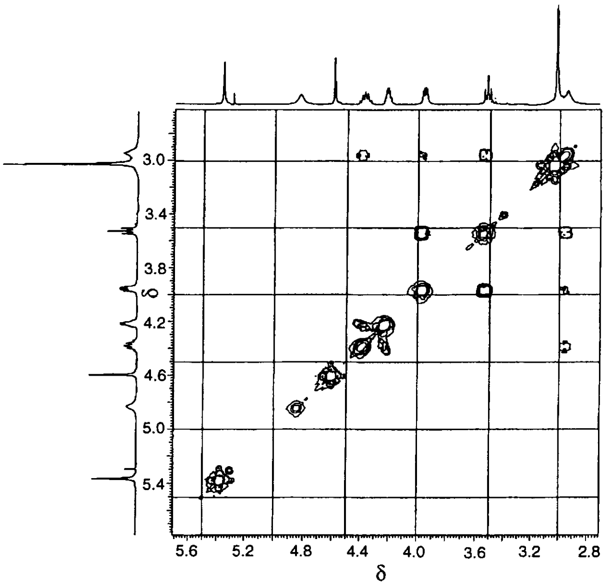

Fig. 1 Part of the ^1H–^1H COSY spectrum of complex **1b** in $CDCl_3$ solution

Table 1 Elemental analysis and some physical data for complexes **1** and **2**

			Analysis^a (%)		IR/cm^{-1}	
Complex	Yield (%)	$[\alpha]_D^{25}$	C	H	ν(Pd–P)	ν(Pd–X)^b
1a	91	62.0 (0.5)^c	58.25 (57.90)	5.25 (5.05)	204w	365m
1b	92	−15.7 (0.5)^c	58.00 (57.90)	5.10 (5.05)	200w	349m
2a·$3H_2O$	85	−11.4 (0.2)^c	58.75 (58.85)	5.65 (5.50)	203w	388m
2b·$3H_2O$	86	32.0 (0.5)^c	58.65 (58.85)	5.45 (5.50)	202w	386m

^{a} Calculated values in parentheses. ^{b} For complexes **1a** and **1b** X = Cl, for **2a** and **2b** X = O. ^{c} Recorded in $CHCl_3$; the values in parentheses are amounts in g per 100 cm^{-3}.

Table 2 Proton NMR data * for the altropyranose ring in complexes **1** and **2** and free HL^1 and HL^2

Compound	H^1	H^2	H^3	H^4	H^5	H^6	H$^{6'}$	PhC*H*	OCH$_3$
HL^1	4.46 (d)	3.23 (m)	4.30 (m)	4.18 (dd)	4.01 (m)	4.35 (m)	3.90 (dt)	5.64 (s)	3.29 (s)
1a	5.39 (s)	4.04 (s)	4.08 (m)	4.34 (m)	1.94 (m)	4.10 (m)	3.04 (dt)	4.82 (s)	3.29 (s)
2a	4.10 (m)	3.80 (m)	4.15 (m)	3.72 (m)	4.12 (m)	4.25 (m)	3.69 (m)	5.58 (s)	3.03 (s)
HL^2	4.49 (s)	3.52 (m)	3.49 (m)	4.44 (m)	4.58 (m)	4.26 (dd)	3.78 (dt)	5.46 (s)	3.44 (s)
1b	4.59 (s)	4.83 (s)	4.22 (m)	4.37 (m)	2.93 (m)	3.95 (dd)	3.53 (dt)	5.35 (s)	3.01 (s)
2b	4.78 (m)	4.37 (m)	3.50 (m)	4.00 (m)	3.48 (m)	4.17 (m)	3.47 (m)	5.16 (s)	3.53 (s)

* Compounds HL^1, HL^2, **1a** and **1b** in CDCl$_3$, **2a** and **2b** in CD$_3$OD. Chemical shifts are expressed in ppm downfield from internal SiMe$_4$ as positive values.

Table 3 Phosphorus-31 * and selected ^{13}C NMR data

Compound	P	C^1	C^2	C^3	C^4	C^5	C^6	Ph*C*H	O*C*H$_3$
HL^1	−16.9	99.8	44.5	58.5	77.3	66.9	69.2	102.0	55.4
1a	21.4	99.7	40.9	56.9	65.7	75.8	69.1	101.9	55.9
2a	49.8	100.9	53.4	72.4	81.4	66.0	70.9	102.9	54.9
HL^2	−21.7	101.2	69.8	41.3	77.0	60.8	69.2	101.4	54.7
1b	21.9	100.8	71.8	38.6	76.8	59.0	69.4	101.2	55.7
2b	52.4	101.0	74.8	52.2	77.3	63.6	70.2	101.8	56.5

* External 85% H$_3$PO$_4$ as standard. Solvents used as in Table 2.

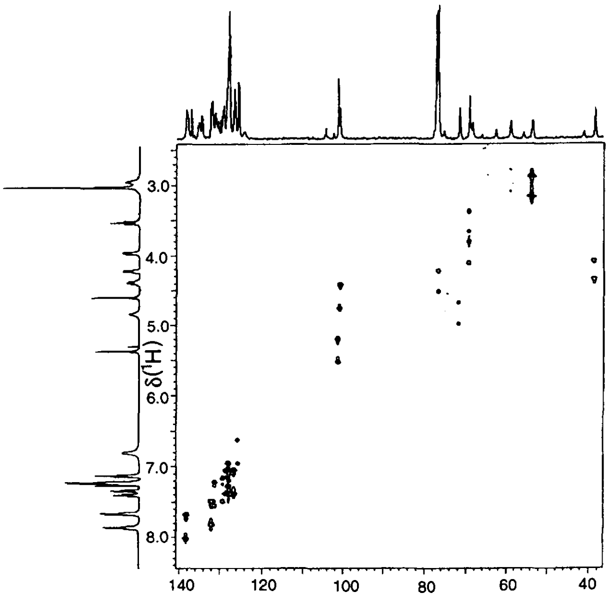

Fig. 2 Partial ^{1}H–^{13}C HMQC spectrum of complex **1b**

presented. Two-dimensional NMR measurements are necessary in order fully to assign the spectra, since the ^{1}H and ^{13}C resonances of the altropyranose ring vary significantly when phosphorus and oxygen atoms ligate to palladium as can be seen from Table 2 and 3.

The ^{1}H–^{1}H COSY spectrum of complex **1b** (Fig. 1) shows no doublet for H^1, and the protons of the pyranose ring cannot be assigned. The signal of C^6 at δ 69.4 was assigned first by DEPT (distortionless enhancements by polarization transfer) techniques, and the signals at δ 3.95 and 3.53 correlating to it in the ^{1}H–^{13}C HMQC spectrum (Fig. 2) were assigned to H^6 and H$^{6'}$, respectively. Returning to the COSY spectrum, H^5 was assigned to the signal at δ 2.93, which is correlated to both H^6 and H$^{6'}$ and H^4 at δ 4.37 and H^3 at δ 4.22. The correlations of H^3–H^2 and H^2–H^1 were not observed since H^3, H^2 and H^1 are all in equatorial positions, even though the correlation of H^1–H (OCH$_3$) had been shown weakly. In comparison to the spectrum of free HL^2, the signal at δ 4.59 was assigned to H^1 and that at δ 4.83 to H^2. When the protons of the pyranose ring have been assigned, the carbon atoms can be assigned easily by use of the ^{1}H–^{13}C HMQC spectrum.

The co-ordination shifts of 0.81 ppm for H^2 of complex **1a** and 0.73 ppm for H^3 of **1b** are large as expected, while the shifts of −1.65 and 2.05 ppm respectively for H^5 are the largest. The ^{13}C chemical shifts vary non-uniformly from HL^1 to **1a** and HL^2 to **1b**. Such a variation of the chemical shifts of **1a** and **1b** suggests that the conformations of the altropyranose rings have changed on co-ordination since Pd^{II} perturbs the electron distribution of the phosphinoaltrose locally at the carbon atom linked directly to the phosphorus atom.

Compounds **1a** and **1b** react with NaOMe in methanol to give the bis(alkoxo)palladium(II) complexes *cis*-[PdL$_2$] (L = L^1 **2a** or L^2 **2b**) in high yields. The ^{31}P-{^{1}H} resonances at δ 49.8 for **2a** and δ 52.4 for **2b** are comparable to the values of δ 44.6–56.4 for *cis*-[PdL$_2$] **4** (L = Ph$_2$PCH$_2$CRR'OH, R = R' = H or Me; R = H, R' = Me),[13] typical for a phosphorus atom ligated to a metal forming a five-membered chelate ring.[25] The ν(Pd–Cl) bands are not present in the spectra of **2a** and **2b**, as expected, and new absorption peaks at 388 and 386 cm^{-1} with medium intensity appear in the far-infrared region. Although there are no similar ν(Pd–O) values of alkoxopalladium(II) complexes for comparison, the new peaks falling in the range 395–340 cm^{-1} for ν(Pd–O) of [Pd$_3$(O$_2$CMe)$_6$],[26] [NEt$_4$]$_2$[Pd$_2$(sp)$_2$(Hsp)$_2$] (H$_2$sp = 2-sulfanylphenol),[27] and [Pd(spo)$_2$] (Hspo = 2-sulfanylpyridine *N*-oxide),[27] are reasonably ascribed to the ν(Pd–O) vibration.

When *trans*-[PdCl$_2$(PR$_3$)$_2$] complexes are dissolved in polar solvents, which are expected to favour isomerization to the *cis* isomers, *cis*-[PdCl$_2$(PR$_3$)$_2$] form even in the dark.[28–31] Compounds **4** isolated from MeOH have thus been assigned a *cis* geometry.[13] Assignment of *cis* geometry to **2a** and **2b** remains tentative since the ligands are bulky, even though their ^{31}P-{^{1}H} NMR data are consistent with those of **4** with *cis* geometry. The asymmetric P–C deformation mode at *ca.* 540 cm^{-1} has been used to assign the stereochemistry of palladium complexes.[18–20] These bands are very weak (relative to the band at *ca.* 620 cm^{-1} for comparison) in the Raman spectra of *cis* complexes and very strong for the *trans* ones.[20] As can be seen from Fig. 3, the intensity of the starred bands at *ca.* 530 cm^{-1} for **1a** [Fig. 3(*b*)] and for **1b** [Fig. 3(*e*)] are nearly equivalent to those at *ca.* 620 cm^{-1}. However, for **2a** [Fig. 3(*c*)] and **2b** [Fig. 3(*f*)], those at *ca.* 530 cm^{-1} are much weaker than at *ca.* 620 cm^{-1}. This fact suggests that the geometry of compounds **2a** and **2b** is *cis*.

Bis(alkoxo)palladium(II) complexes **2a** and **2b** in the solid state are remarkably stable to air and water, and also thermally. During the NMR measurements the colourless solution of **2a** in

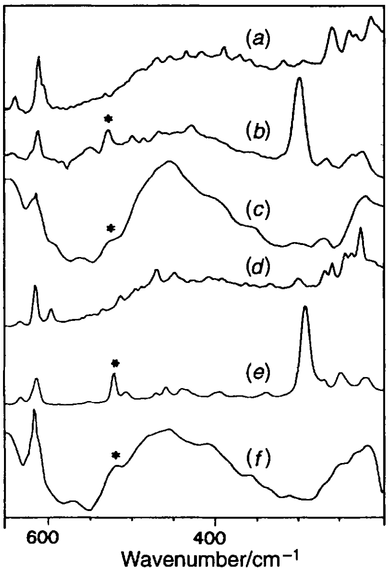

Fig. 3 The partial Raman spectra of compounds HL^1 (*a*), **1a** (*b*), **2a** (*c*), HL^2 (*d*), **1b** (*e*) and **2b** (*f*)

$CDCl_3$ darkened after a few minutes whilst in CD_3OD the solution was stable for several hours; **2b** is stable in both $CDCl_3$ and CD_3OD for several days.

The assignments of the ^1H and ^{13}C NMR spectra of compounds **2a** and **2b** were made similarly to that of **1b** with the help of ^1H–^1H COSY and ^1H–^{13}C HMQC techniques. The data (Tables 2 and 3) vary significantly from those of **1a** and **1b**, respectively. In addition, the correlations of H^3–H^2 and H^2–H^1 are apparent indicating that the conformation of the pyranose ring differs from that in **1**, and that the atoms H^1–H^3 tend to be in axial positions. Except for the co-ordination shifts arising from the oxygen atom co-ordinated to palladium(II), the changes are attributed to the fact that the phosphorus and oxygen donor atoms must twist closely toward each other in order to co-ordinate to the palladium simultaneously to form **2a** and **2b**, thus making the conformation of the altropyranose ring change significantly.

Crystal structure of compound 1b

The crystal structure (Fig. 4) and absolute configuration determination unequivocally confirms the *trans* geometry of complex **1b**. Selected atomic distances and angles are given in Table 4. The palladium atom occupies a special position on a crystallographic two-fold axis which forces the mononuclear complex to assume a perfect C_2 arrangement, and deviates 0.21 Å from the plane formed by the atoms P, P′, Cl and Cl′. The apparent deviations from the ideal square-planar configuration can be primarily attributed to the overcrowding caused by the bulky phosphine ligands, although *trans* to each other. This accounts for the fact that the angle P–Pd–P′ is 165.38(4)° and P–Pd–C(21) is 119.8(1)° to reduce steric interaction. In order to accommodate the bulky phosphine ligands, the chlorine atoms are forced close together as indicated by the angle Cl–Pd–Cl′ 174.05(6)°. The Pd–Cl [2.3090(8) Å] and Pd–P [2.3314(9) Å] distances are slightly longer than those found in *trans*-$[PdCl_2L_2]$ [$L = Ph_2PCH_2C(O)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$][21] [2.287(1) and 2.314(1) Å, respectively], and this may also be a consequence of the overcrowding.

As can be seen from Fig. 4, both the pyranose ring and the 4,6-*O*-benzylidene ring adopt distorted chair conformations, similar to those of free HL^2.[14] The average torsion angles[32] of the pyranose ring and the 4,6-*O*-benzylidene ring are ± 53.5 and ± 57.4° for **1b**, and ± 55 and ± 60° for HL^2, respectively. The torsion angles P–C(3)–C(2)–O(2) and O(2)–C(2)–C(1)–O(1) are 149.6 and −149.6°, smaller than 164.7 and 163.5° of free HL^2, respectively, indicating that the diphenylphosphino, OH and OMe groups are all in pseudo-axial positions.

The distance between the atom O(2) and the O(6′) of another molecule is 3.148(5) Å, indicating a weak intermolecular hydrogen bond. The packing diagram of molecule in the lattice is shown in Fig. 5.

Table 4 Selected atomic distances (Å) and angles (°) with estimated standard deviations in parentheses for complex **1b**. The primes denote the corresponding positions related by the symmetry operation $-x$, $+y$, $-z + \frac{1}{2}$ of the crystallographic two-fold axis

Pd–Cl	2.3090(8)	Pd–P	2.3314(9)
P–C(3)	1.860(3)	P–C(15)	1.825(4)
P–C(21)	1.819(3)	C(1)–C(2)	1.523(6)
C(2)–C(3)	1.541(5)	C(3)–C(4)	1.517(5)
C(4)–C(5)	1.517(5)	C(5)–C(6)	1.504(6)
C(1)–O(1)	1.391(4)	C(1)–O(5)	1.414(5)
C(2)–O(2)	1.436(5)	C(4)–O(4)	1.416(5)
C(5)–O(5)	1.425(5)	C(6)–O(6)	1.444(6)
C(7)–O(4)	1.417(5)	C(7)–O(6)	1.409(5)
C(8)–O(1)	1.424(6)	O(2) ··· O(6′)	3.148(5)
Cl–Pd–Cl′	174.05(6)	Cl–Pd–P	86.62(3)
Cl′–Pd–P	92.62(3)	P–Pd–P′	165.38(4)
Pd–P–C(11)	99.7(1)	Pd–P–C(21)	119.8(1)
Pd–P–C(3)	114.6(1)	P–C(11)–C(12)	115.5(3)
P–C(11)–C(16)	125.4(3)	P–C(21)–C(22)	120.4(3)
P–C(21)–C(26)	120.1(3)	P–C(3)–C(2)	115.2(2)
P–C(3)–C(4)	118.7(3)	C(3)–P–C(11)	106.8(2)
C(3)–P–C(21)	109.8(2)	C(11)–P–C(21)	104.1(2)
C(1)–C(2)–C(3)	113.7(4)	C(2)–C(3)–C(4)	108.0(3)
C(3)–C(4)–C(5)	113.0(3)	C(4)–C(5)–C(6)	108.3(3)
C(1)–O(1)–C(8)	113.6(4)	C(1)–O(5)–C(5)	112.9(3)
C(2)–C(1)–O(1)	106.8(3)	C(2)–C(1)–O(5)	113.4(3)
O(2)–C(2)–C(1)	108.5(3)	O(2)–C(2)–C(3)	108.1(3)
C(3)–C(4)–O(4)	112.2(3)	C(5)–C(4)–O(4)	110.3(2)
C(5)–C(6)–O(6)	110.0(4)	C(6)–O(6)–C(7)	112.1(4)
O(6)–C(7)–O(4)	111.5(3)	C(4)–O(4)–C(7)	111.3(3)

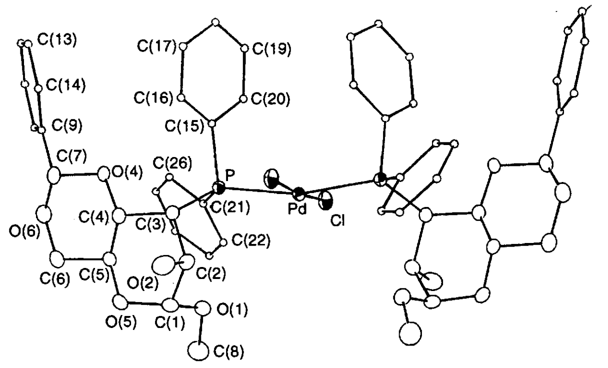

Fig. 4 View of the molecular unit of complex **1b** showing the numbering scheme

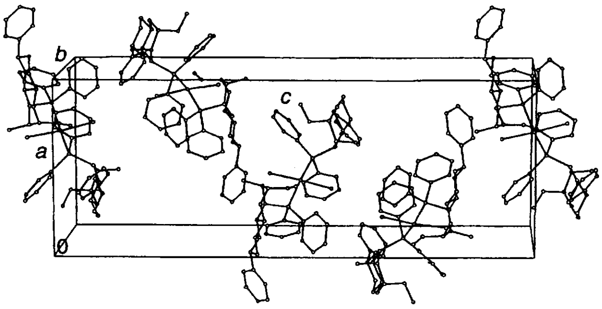

Fig. 5 Packing of complex **1b** in the lattice

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