Platinum(II) and Palladium(II) Complexes of Cholesteryl Diphenyl- and Diethyl-phosphinite; the X-Ray Structure of Bis(cholesteryl diethylphosphinite)-dichloropalladium(II)

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Palladium(II) and platinum(II) complexes of cholesteryl diphenylphosphinite, PPh_2(O-chl), and cholesteryl diethylphosphinite, PEt_2(O-chl), have been synthesised; the X-ray structure of $[PdCl_2\{PEt_2(O\text{-chl})\}_2]$ shows that though the phosphinites are *trans*-, the cholesteryl substituents are folded back in the same direction.

In our search for ligand systems that can confer novel and useful properties on metal complexes,[1] we became intrigued by the hitherto little-explored liganding possibilities of steroid-derived phosphines and phosphites. Complexes based on such ligands ought to have wide applicability as interesting materials with unusual optical and electronic properties, and should also be capable of promoting asymmetric organic reactions. We report here our first synthetic success in this area: the preparation of two phosphinite ligands, based on cholesterol, and of the derived palladium(II) and platinum(II) complexes, as well as the X-ray crystal structure of one of them. Only a few simple alkyl diphenylphosphinite [$PPh_2(OR)$, R = Me, Et, Bu] complexes (of Pt, Rh, Ru, and Mn) have yet been reported[2] and there do not seem to be any X-ray data.

The ligand, PPh_2(O-chl), **1a**, was made by dropwise addition of a solution of chlorodiphenylphosphine (0.45 cm^3, 2.5 mmol) in THF (25 cm^3) to a solution of cholesterol (Aldrich; 1.45 g, 3.75 mmol) and pyridine (3 mmol) in THF (50 cm^3) with exclusion of air.† After stirring (6 h, 20 °C) the solution of the ligand [^{1}H NMR ($CDCl_3$) δ 7.5 (m, 4H), 7.3 (m, 6H), 5.35 (d, 1H), 3.8 (m, 1H), 0.7 to 2.5 (mm 43H); ^{31}P ($CDCl_3$): δ 106] was filtered through Celite into a red toluene solution of $[PdCl_2(PhCN)_2]$ (1 mmol). The toluene solution immediately turned yellow due to the formation of **2a**. Work-up and crystallisation from petroleum ether (bp 40–60 °C) followed by recrystallisation from ethyl acetate gave the pure palladium complex **2a**.‡ The palladium complex **2b**‡ was made from the cholesteryl diethylphosphinite which was obtained *in situ* in a similar manner from cholesterol and chlorodiethylphosphine.

The far IR spectrum of **2b** showed a single ν(Pd–Cl) at 368 cm^{-1} indicating a *trans*-geometry.[3] This was borne out by the X-ray crystal structure of **2b**,§ which showed that the molecule comprises a square-planar palladium(II) carrying two mutually *trans* chloro ligands [Pd–Cl(1), 2.292(6); Pd–Cl(2), 2.276(6) Å] and two mutually *trans* cholesteryl diethylphosphinites [Pd–P(1), 2.346(4); Pd–P(2), 2.332(4) Å]. Somewhat surprisingly, the two cholesteryl substituents are folded back in the same direction and are approximately parallel to each other and perpendicular to the coordination plane on one side of the metal (Fig. 1). This leaves one axial site of the palladium relatively exposed, and the opposite site sterically protected (by the cholesteryls). The small displacement (0.034 Å) of the palladium from the mean P_2Cl_2 plane (rms deviation 0.145 Å) is such as to increase the exposure of the less protected axial site, although the phosphorus atoms lie on the opposite side of this mean plane to the cholesteryl substituents. The square-planar coordination is subject to a significant tetrahedral twist of 10.5° between the two PdPCl planes. The two cholesteryl

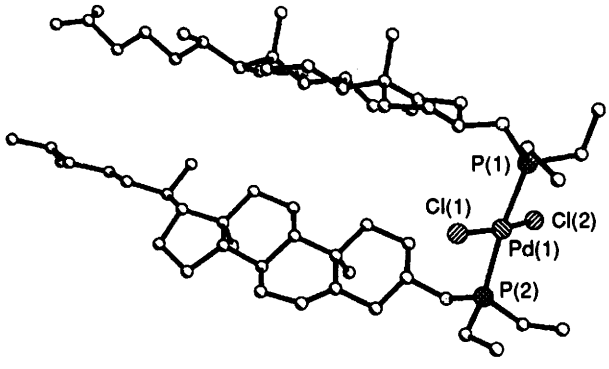
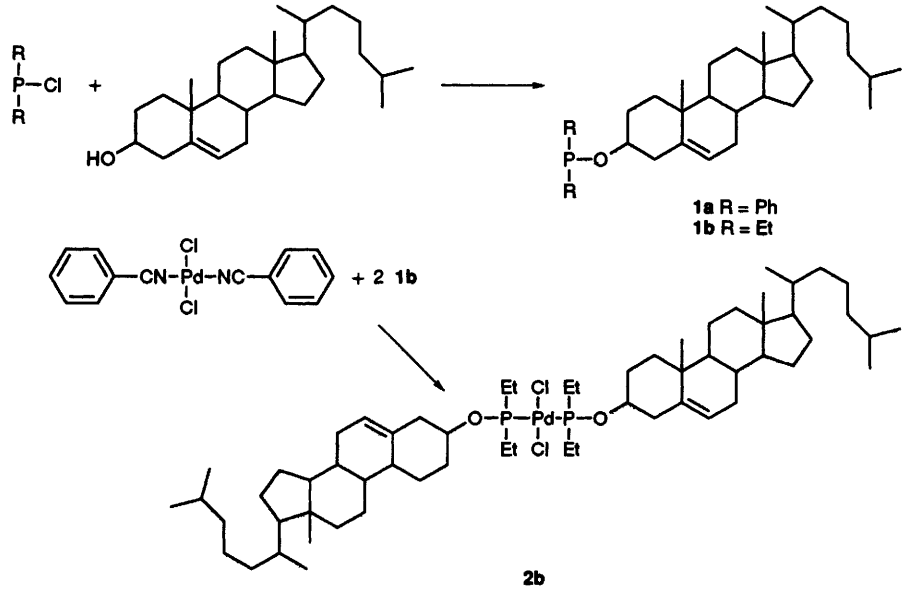


Fig. 1 The X-ray structure of the palladium(II) complex of cholesteryl diethylphosphinite, PEt_2(O-chl), $[PdCl_2\{PEt_2(O\text{-chl})\}_2]$



residues have normal geometries and have retained the stereochemistry found in cholesterol. The terminal chain on the cholesterol has an approximate antiperiplanar conformation, and there is evidence for some disorder of the terminal isopropyl groups, leading to short C–Me bond lengths in the refined model: all other bond lengths are acceptable.

The platinum(II) compounds $[PtCl_2\{PR_2(O\text{-}chl)\}_2]$ **3a**‡ (R = Ph) and **3b**‡ (R = Et) have been synthesised in a similar manner from **1a** or **1b**, and $[PtCl_2(PhCN)_2]$ in dichloromethane solvent. The ^{31}P NMR spectra showed the presence of both the *cis* and *trans* isomers in the crude products which could be separated by column chromatography using dichloromethane as eluent; the *trans* isomer eluted first. When the crude reaction products were heated (toluene or acetone, 2 h) more *cis* isomer was obtained. For both the platinum and the palladium complexes NMR data indicated that crude yields were reasonable (≥50%), but the amounts of analytically pure complexes obtained were significantly lower. Purification methods have not yet been optimised.

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Footnotes

† In the presence of air the compound $O{=}PPh_2(O\text{–chl})$ was formed: ^1H NMR ($CDCl_3$) δ: 7.75 (m, 4H), 7.5 (m, 6H), 5.3 (d, 1H), 4.25 (m, 1H), 0.8 to 2.5 (mm, 43H); ^{31}P NMR ($CDCl_3$) δ: 28.7.

‡ **2a**, decomp 223 °C; 28%. ^1H NMR ($CDCl_3$) δ: 7.75 (m, 4H), 7.35 (m, 6H), 5.1 (d, 1H), 4.15 (m, 1H), 0.65–2.1 (mm, 43H). ^{31}P NMR ($CDCl_3$) δ: 103.7. **2b**, mp 179 °C; 17%. ^1H NMR ($CDCl_3$) δ, 5.35 (m, 1H), 4.2 (m, 1H), 0.6–2.6 (mm, 53H). ^{31}P NMR ($CDCl_3$) δ: 119.1. **3a**, decomp 243 °C; 15%. ^1H NMR ($CDCl_3$) *trans*: δ 7.7 (m, 4H), 7.3 (m, 6H), 5.2 (d, 1H), 4.7 (m, 1H), 0.6 to 2.55 (mm, 43H). ^{31}P NMR ($CDCl_3$) *trans*: δ 94.1, $J_{Pt\text{-}P}$ 2790 Hz; *cis*: δ 77.2, $J_{Pt\text{-}P}$ 4155 Hz. **3b**, mp 193 °C; ^1H NMR ($CDCl_3$) *trans*: δ 5.4 (d, 1H); 4.2 (sept, 1H); 0.6 to 2.55 (mm, 53H). ^{31}P NMR ($CDCl_3$) *trans*: δ 109.5, $J_{Pt\text{-}P}$ 2596 Hz; *cis*: δ 101.8, $J_{Pt\text{-}P}$ 4058 Hz.

In all cases the yields quoted are after purification but are not optimised. Satisfactory microanalysis obtained for all compounds.

§ Crystals of **2b** were grown from ethyl acetate as yellow blocks; crystal dimensions, 0.60 × 0.20 × 0.20 mm. *Crystal data*: $C_{62}H_{110}Cl_2O_2P_2Pd$, M 1126.82; monoclinic, a = 14.970(10); b = 12.097(6); c = 18.310(11) Å; β = 94.11(5)°; U = 3307.4(34) Å^3; Z = 2; D_c = 1.131 g cm^{-3}; space group, $P2_1$ (C_2^2, No. 4), Mo-Kα radiation (λ = 0.71069 Å), μ(Mo-Kα) = 4.41 cm^{-1}, $F(000)$ = 1215.89. Three dimensional room temperature X-ray data were collected in the range $3.5 < 2\theta < 45°$ on a Nicolet R3 diffractometer by the omega scan method. The 2875 independent reflections (of 4836 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of 5 azimuthal scans (minimum and maximum transmission coefficients 0.622 and 0.681). The structure was solved by direct methods and refined by blocked cascade least squares methods. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final R = 0.0713 (R_w = 0.0679; 621 parameters; mean and maximum δ/σ 0.040, 0.145) with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density −0.53 and 0.52 e Å^{-3}. A weighting scheme $w^{-1} = \sigma^2(F) + 0.00125\,(F)^2$ was used in the latter stages of refinement. The correct enantiomeric form of the cholesterol fragment was consistent with the marginally lower R (by 0.0005) of the reported structure. Complex scattering factors were taken from reference 4 and from the program package SHELXTL[5] as implemented on the Data General DG30 computer. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

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