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The first transition metal cholesteryl-phosphine complexes

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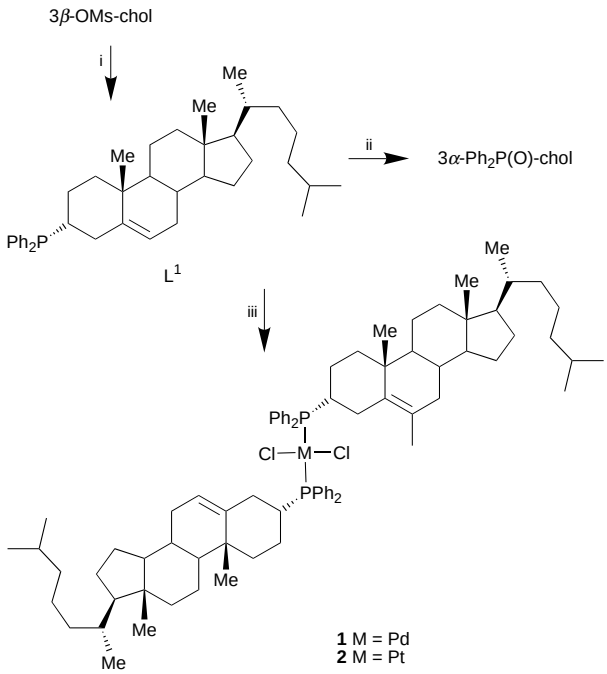
Novel optically pure cholesteryl-phosphine ligands (3α-PPh_2chol and 3β-PMe_2chol) have been synthesized and were shown to form stable and highly soluble Pd(II) and Pt(II) complexes; as revealed by an X-ray analysis the (chol)-P···P(chol) fragment of the square planar *trans*-[PtI_2(3β-PMe_2chol)$_2$] complex adopts a staggered arrangement (V-shape).

As part of our ongoing research for new catalytic and mesomorphic molecular materials it was of interest to design multifunctional ligands based on steroidal phosphines. Surprisingly, very little work has been devoted to cholesteryl-derived phosphines[1] and it appears that no complexes have been reported until now with such hybrid ligands. The cholesteryl fragment offers many advantages in terms of chirality,[2] liquid-crystalline behaviour,[3] lipophilicity,[4] optical and molecular recognition.[5] We now report a convenient synthesis of 5-cholestene derivatives substituted at the C_3-carbon atom with phosphino groups (PPh_2 and PMe_2) and present their coordinative properties towards precious metals.†

Phosphine L^1 was prepared in 73% isolated yield‡ by reacting 5-cholestene-3β-methanesulfonate (3β-MsO-chol)[6] with Ph_2PLi as shown in Scheme 1. The ligand is characterized by a ^{31}P NMR signal at δ −18.6 and by an $[\alpha]_D^{589}$ of +15.8° (*c* = 1, CH_2Cl_2). The phosphino subunit occupies the α position of the C_3-carbon atom as unambiguously proven by a positive NOE effect of 8% found between the olefinic H-6 proton and the *ortho* P-phenyl atoms. It is noteworthy that there is no indication for the formation of the 3β substituted isomer, an observation that is in keeping with an S_N2 substitution reaction. A complete assignment of proton and carbon signals was made using NOESY, ^1H–^{13}C COSY, ^{13}C-DEPT and HMBC pulse sequences (for selected data and atom labelling see Table 1). The corresponding phosphine oxide which was readily obtained by oxidation is characterised by a ^{31}P NMR signal at δ +35.6, and a strong IR absorption band at 1187 cm^{-1} ($\nu_{P=O}$). Reaction of 2 equiv. of L^1 with [MCl_2(PhCN)$_2$] afforded quantitatively‡ the corresponding *trans*-[$MCl_2(L^1)_2$] complexes (**1** M = Pd, **2** M = Pt; Scheme 1). Both complexes are *highly* soluble in *hydrocarbons* and insoluble in protic solvents.

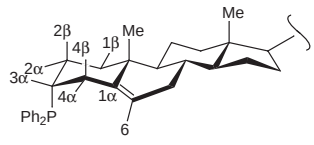


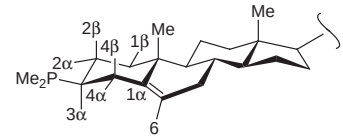
Scheme 1 *Reagents and conditions*: i, Ph_2PLi, THF, 25 °C, 3 d; ii, air, CH_2Cl_2; iii, [$MeCl_2$(PhCN)$_2$], CH_2Cl_2 (M = Pd, Pt).

In contrast to the reaction described above yielding exclusively a C_3-α-substituted product, we discovered that treatment in THF at −78 °C at 3β-Cl-chol with 2 equiv. of PMe_2K (prepared[7] by quantitative reduction of Me_2P–PMe_2 in decaline) gave a mixture of compounds from which 3β-PMe_2-chol (L^2) could be isolated in 47% yield (as the major compound, Scheme 2). Selected spectroscopic data for L^2 are: δ_P −41 and $[\alpha_D]^{589}$ of −33.7° (*c* = 1, CH_2Cl_2). The α-stereochemistry of L^2 could unequivocally be established using 2D proton NMR spectroscopy ($^3J_{H\text{-}3\alpha/H\text{-}4\beta}$ 11 Hz and $^3J_{H\text{-}3\alpha/H\text{-}4\alpha}$ 15 Hz) and was further confirmed by an X-ray diffraction study (*vide infra*). The 3α-PMe_2-chol isomer was also formed in this reaction (β/α ratio 7/3) but could not be obtained in a pure form. Note, the ^{31}P NMR signal of the latter isomer (δ_P −54) is considerably shifted with respect to the β form; such shielding effects have previously been observed on going from 4-methyl-$P_{axial}Me_2$-cyclohexane to its $P_{equatorial}$-isomer.[8] We also note that Me_2P–PMe_2 (δ_P −58) was detected in the reaction mixture.

The sparingly soluble complexes **3** (M = Pd) and **4** (M = Pt) were obtained in high yield by reaction of L^2 with [$MCl_2(SEt)_2]_2$. Metathesis of **4** with NaI in acetone–THF resulted in the formation of the soluble *trans*-[$PtI_2(L^2)_2$] complex **5** (Scheme 2), the molecular structure of which was determined by a single-crystal X-ray analysis¶ (Fig. 1). This study confirmed the α-stereochemistry of the cholesteryl-phosphine ligand L^2. The platinum atom is in a square-planar environment with the two P-atoms occupying *trans* positions. Interestingly, the molecule possesses a C_2-axis perpendicular to the metal plane, with the two steroidal backbones located on the same side of the coordination plane. Observing the molecule perpendicularly to the P···P axis, the two chol subunits adopt a V-shaped arrangement, as shown in Fig. 1; the relative organization of the steroidal fragments is probably controlled by van der Waals forces between cholesteryl units of neighboring molecules. In the crystallographic cell (Fig. 1) the molecules are arranged in a head-to-tail fashion, a situation which is reminiscent of that found in some chol-derivatives displaying liquid-crystalline behaviour.[3] The shortest chol–chol intermolecular distances are in the order of 2.5 Å (1 − *x*, 1 − *y*, *z*). Note, the situation found here contrasts with the solid state

Table 1 Selected NMR data [^{1}H(500 MHz), ^{13}C{^{1}H} (125 MHz), $CDCl_3$] for L^1 and L^2





C atom		δ_C (J/Hz)	δ_H (J/Hz)	δ_C (J/Hz)	δ_H (J/Hz)
1	CH_2	34.99 (d, $^3J_{CP}$ 10)	1.59 (β), 1.82 (α)	40.28 (d, $^3J_{CP}$ 13)	1.08 (β), 1.92 (α)
2	CH_2	24.15 (d, $^2J_{CP}$ 12)	1.58 or 1.94 (α),[a] 1.97 (β)	24.95 (d, $^2J_{CP}$ 13)	1.39 (β), 1.64 (α)
3	CH	35.05 (d, J_{CP} 9)	2.72 (β)	40.88 (d, J_{CP} 8)	1.18 (α)
4	CH_2	33.94 (d, $^2J_{CP}$ 15)	1.91 (α), 2.66 (β)	35.03 (d, $^2J_{CP}$ 13)	2.03 (α), 2.13 (β)
5	C	140.03 ($^3J_{CP}$ 0)		142.85 (d, $^3J_{CP}$ 11)	
6	CH	121.96	5.17 (br d, $^3J_{HH}$ 5.0)	119.63	5.30 (d, $^3J_{HH}$ 5.0)
	PCH_3			11.46 (d, J_{CP} 14)	1.00 (d, $^2J_{HP}$ 1.9)
	PCH_3			11.38 (d, J_{CP} 14)	0.99 (d, $^2J_{HP}$ 2.0)

[a] Tentative assignment.

structure of a related bis(cholesteryldiethylphosphinite)Pd(II) complex where no significant intermolecular interactions were observed.[2c]

In summary, chol-derived phosphines with a wide range of physical properties should now be accessible with this synthetic protocol. Further studies are in progress to elucidate the mechanism and driving force leading to the formation of the new 3β-PMe_2chol ligand. We are also continuing to explore the potential of these new ligands in three major directions: (i) formation of three-dimensional scaffoldings to generate metallomesogens, (ii) the use of these functional phosphines for Wittig olefinations and finally (iii) the study of their transition metal complexes as precursors in asymmetric catalysis.

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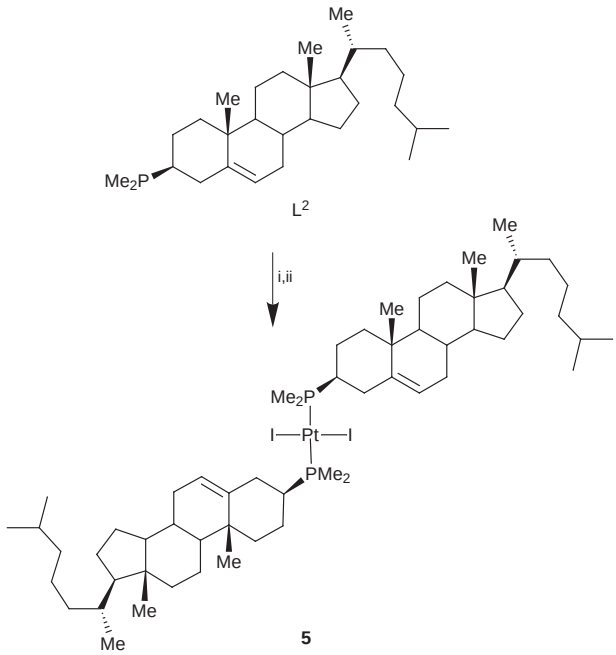

Scheme 2 *Reagents and conditions*: i, $[PtCl_2(SEt_2)_2]$, THF; ii, NaI, acetone–THF.

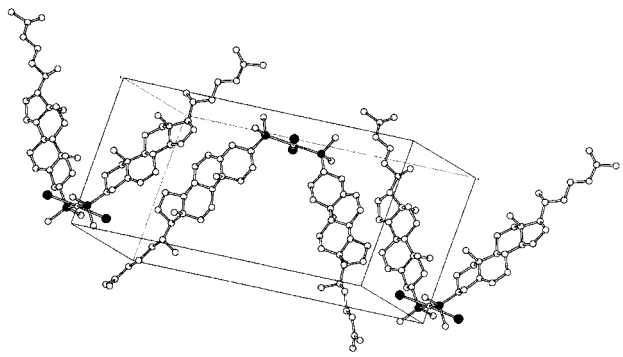

Fig. 1 Solid state structure of complex **5** showing the organization of the cholesteryl fragments. Selected bond lengths (Å): Pt–I 2.584(1), Pt–P 2.332(3), P–C(1) 1.81(2), P–C(2) 1.82(2), P–C(3) 1.85(1).

Notes and references

† On the basis of spectroscopic evidence, including EI and FABMS and elemental analysis the structures of the new ligands and complexes were unequivocally authenticated. See http://www.rsc.org/suppdata/cc/1999/393/ for selected data for L^1, 3α-$Ph_2P(O)$chol, L^2 and **1**–**5**.

‡ Obtained by precipitation with MeOH: L^1 was recrystallized from Et_2O–MeOH and complexes **1** and **2** were obtained analytically pure after precipitation.

¶ *Crystal data* for **5**•2$CHCl_3$•H_2O: $C_{58}H_{102}P_2I_2Pt$•2$CHCl_3$•H_2O, M = 1567.08, orthorhombic, space group $P2_12_12$, yellow crystals, a = 29.557(1), b = 9.069(3), c = 12.422(4), V = 3329.7 Å^3, Z = 2, D_c = 1.563, μ = 14.161 mm^{-1}, $F(000)$ = 1580. Data were collected on a Philips PW1100/16 diffractometer (graphite Cu-Kα radiation, 1.5418 Å) at −100 °C. 2353 reflections collected ($3 \leqslant 2\theta \leqslant 54°$), 2143 data with $I > 3\sigma(I)$. The structure was solved using the Nonius OpenMoleN[10] package and refined by full matrix least-squares with anisotropic thermal parameters for all non hydrogen atoms except for the solvent molecules (the latter are disordered in the crystallographic structure). The absolute configuration was determined by refining Flack's x parameter equal to 0.02(2). Final results: $R(F)$ = 0.046, $wR(F)$ = 0.066, GOF = 1.029, 310 parameters, largest difference peak = 1.037 e Å^{-3}. CCDC 182/1143. See http://www.rsc.org/suppdata/cc/1999/393/ for crystallographic files in .cif format.

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