1,2-Bis[2-(2,4,6-tri-*tert*-butylphenyl)phosphanediylmethyl]benzene, L: synthesis and structure of L, of the chelated complex [$PdLCl_2$] and of a derived cyclometallated chiral complex

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The synthesis and crystal structure of 1,2-bis[2-(2,4,6-tri-*tert*-butylphenyl)phosphanediylmethyl]-benzene, L, are reported as well as the preparation and conformation of the novel seven-membered ring complex [$PdLCl_2$]; this complex reacts with alcohols (MeOH, EtOH) to give a chiral cyclometallated complex [*rac* (*R*)P, (*R*)C; (*S*)P, (*S*)C] where the metal is bound to both a phosphaalkene and a phosphite phosphorus atom.

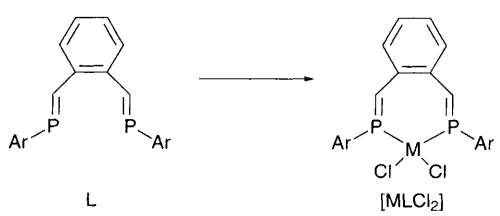
Although imines are widely used for cyclometallation with palladium and platinum and have been extensively investigated in the context of the activation of C–H bonds,[1] the coordination chemistry of their phosphorus analogues, the phosphaalkenes, has received much less attention. Compounds containing a C=P bond are generally very reactive[2] and their ability to form stable chelates with platinum(II) and palladium(II) ions has been recognized only very recently.[3] Due to the opposite polarity of the C=P and C=N bonds, imine and phosphaalkene coordination centres are expected to exhibit significant chemical differences and, as shown below, this property can be used to form new chiral complexes.

In the present communication, we report the synthesis† and the crystal structure‡ of the novel bidentate ligand L which forms complexes [$MLCl_2$] (M = Pd, Pt)§ (Scheme 1).

In the crystal‡ [Fig. 1(*a*)] L adopts the *E,E* conformation but the phosphorus atoms are located above and below the plane of the central phenyl ring [+0.872(6), −0.790(6) Å].

Seven-membered ring complexes have already been described for diphosphine ligands[9] but, as far as we know, such complexes have never been reported for diimines or diphosphaalkenes. The X-ray structure of {1,2-bis[2-(2,4,6-tri-*tert*-butylphenyl)phosphanediylmethyl-κ*P*]benzene}-*cis*-dichloropalladium, [$PdLCl_2$]‡¶ [Fig. 1(*b*)] indicates that the coordination of the metal is square planar (maximum deviation of the mean plane passing through the Pd, P and Cl atoms 0.026 Å) with P–M–P 92.2(5)°. The coordination plane makes an angle of 24.2(3)° with the central phenyl ring and the orientation of the P–Ar bonds, below the coordination plane [Cl(1)–Pd–P(1)–C(9) 12.7(4), Cl(2)–Pd–P(2)–C(15) −9.0(5)°], involves a pseudo-mirror plane bisecting the P–Pd–P bond angle.

For [$PdLCl_2$] nucleophilic addition is expected to occur on the phosphorus atom. This is indeed observed with methanol or ethanol as reactant, this addition of the alkoxy group on the phosphorus atom is then followed by elimination of HCl and by the formation of a carbon–metal bond.‖



L [$MLCl_2$]

Scheme 1 Ar = $C_6H_2Bu^t_3$-2,4,6; M = Pd, Pt

To our knowledge, this reaction (Scheme 2) has never been reported for phosphaalkene ligands. As shown by the crystal structure‡ [Fig. 1(*c*)] of the resulting complex

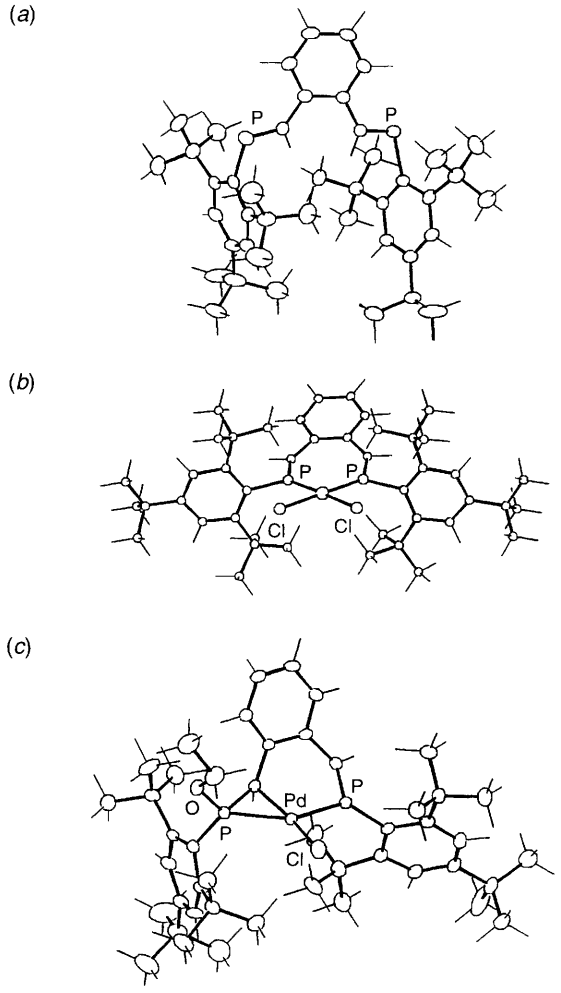
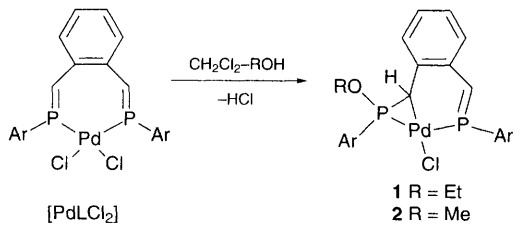


Fig. 1 Perspective views of the crystal structures of L (*a*), [$PdLCl_2$] (*b*) and **1** (*c*). For **L** and **1** ellipsoids are represented with 50% probability.



[$PdLCl_2$]

1 R = Et
2 R = Me

Scheme 2

1, {1-[2-(2,4,6-tri-*tert*-butylphenyl)-2-ethoxyphosphanemethyl-κ²*CP*] 2-[2-(2,4,6-tri-*tert*-butylphenyl)phosphanediylmethyl-κ*P*]benzene}chloropalladium, the metal atom is incorporated in both a three- and a six-membered ring and is coordinated to two phosphorus atoms of different functionality (phosphite and phosphaalkene). The Pd, P and Cl atoms are coplanar (maximum deviation 0.003 Å) and the carbon bonded to the Pd atom is located at 0.368 Å from this plane. It should be noted that the attack of RO^- is regio- and stereo-selective and thus complex **1** is chiral. As shown by the crystal structure, the asymmetric carbon and phosphorus atoms have the same relative configuration; the complex is obtained as a racemic compound [(*R*)P, (*R*)C; (*S*)P, (*S*)C]. The fact that only these two stereoisomers are formed is due to steric interactions in [$PdLCl_2$] (see above the orientation of the P–Ar bonds) which imply that additions to the phosphorus atoms occur *syn* to the central phenyl ring. Complexes having a structure similar to that of **1** might be interesting catalysts for enantioselective reactions.

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Footnotes

† L was prepared following a method similar to that previously reported for the synthesis of 1,3-bis[2-(2,4,6-tri-*tert*-butylphenyl)phosphanediylmethyl]benzene.[3] Only one isomer (*E,E*) was detected and isolated [mp 115–117 °C; $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ 263.7]. As shown by ^{31}P NMR, irradiation (mercury lamp) of a solution of this isomer in benzene led to a mixture of *E,E,E,Z* and *Z,Z* isomers.

‡ *Crystallographic data*: Cell dimensions and intensities were measured at 180 K {L and [$PdLCl_2$]} and 190 K (**1**) on a Nonius CAD4 diffractometer with graphite-monochromated Cu-Kα radiation (λ = 1.5418 Å), ω–2θ scans, scan width 1.5° + 0.14 tanθ, scan speed 0.09° s^{-1}. Two reference reflections measured every 45 min showed variations less than 3.2σ(*I*) (L and **1**). The structures were solved by direct methods using MULTAN 87,[4] all other calculations used XTAL system[5] and ORTEP[6] programs. Atomic scattering factors and anomalous dispersion terms were taken from ref. 7. Data were corrected for Lorentz and polarization effects and for absorption[8] (L and **1**). Refinements (on *F*) were performed with full-matrix least squares using weights of $1/\sigma^2(F_o)$ (L and **1**).

Ligand L: $C_{44}H_{64}P_2$, *M* = 654.9, triclinic, space group $P\bar{1}$, *a* = 10.0786(5), *b* = 11.8789(6), *c* = 17.909(1) Å, α = 79.492(4), β = 76.654(2), γ = 89.135(4)°, *U* = 2050.4(2) Å³ (by least-squares refinement of 25 reflections, 30 < 2θ < 76°), μ = 1.147 mm^{-1} (A^*_{min} = 1.219, A^*_{max} = 1.319), *F*(000) = 716, D_c = 1.06 g cm^{-3}, *Z* = 2. Colourless prism, 0.20 × 0.24 × 0.25 mm mounted on a quartz fibre. 4192 unique reflections measured (6 < 2θ < 100°; −9 < *h* < 9, −11 < *k* < 11, 0 < *l* < 17) of which 3777 were considered observed [$|F_o| > 4\sigma(F_o)$]. Final values; *R* = 0.050, R_w = 0.041 and S = 3.64 for 429 variables and 3777 contributing reflections. All coordinates of hydrogen atoms were calculated. For one *tert*-butyl substituent, two staggered positions were observed with refined populations of 79.1(7) and 20.9(7)%. The atomic sites of the minor conformation was refined with isotropic displacement parameters. Residual extrema: +0.29, −0.28 e $Å^{-3}$.

[$PdLCl_2$]: $C_{44}H_{64}Cl_2P_2Pd{\cdot}CH_2Cl_2{\cdot}3CH_3CH_2OH$, *M* = 1067.4, monoclinic, space group $P2_1/c$, *a* = 20.451(2), *b* = 11.114(1), *c* = 26.066(4) Å, β = 111.896(5), *U* = 5497(1) Å³ (by least-squares refinement of 22 reflections, 38 < 2θ < 60°), μ = 5.471 mm^{-1}, *F*(000) = 2256, D_c = 1.29 g cm^{-3}, *Z* = 4. Fragile red needles. Because of crystal decomposition, only a *partial* data collection (*l* < 24) was performed. 7521 measured reflections (4 < 2θ < 110°; −21 < *h* < 21, 0 < *k* < 11, 0 < *l* < 24) of which 6545 were unique and 5267 considered observed [$|F_o| > 4\sigma(F_o)$]. Final values; *R* = R_w = 0.082 (*w* = 1), and *S* = 7.21 for 544 variables. The three EtOH guest molecules are disordered.

Complex **1**: $C_{46}H_{69}ClOP_2Pd$, *M* = 841.9, triclinic, space group $P\bar{1}$, *a* = 10.3887(9), *b* = 15.044(2), *c* = 15.535(2) Å, α = 100.022(5), β = 100.024(6), γ = 105.522(5)°, *U* = 2240.5(5) Å³ (by least-squares refinement of 20 reflections, 55 < 2θ < 76°), μ = 4.792 mm^{-1} (A^*_{min} = 1.880, A^*_{max} = 4.101), *F*(000) = 892, D_c = 1.25 g cm^{-3}, *Z* = 2. Red prism, 0.16 × 0.26 × 0.38 mm mounted on a quartz fibre. 6605 unique reflections measured (6 < 2θ < 120°, −11 < *h* < 11, −16 < *k* < 16, 0 < *l* < 17) of which 6317 were considered observed [$|F_o| > 4\sigma(F_o)$]. Final values; *R* = 0.037, R_w = 0.039 and *S* = 4.26 for 496 variables and 6317 contributing reflections. All non-methyl hydrogen atoms were observed and refined. Residual extrema: +1.21, −0.99 e $Å^{-3}$.

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.

§ Ligand L was treated with 1 equiv. of [$Pd(NCPh)_2Cl_2$] in CH_2Cl_2 at room temp. to give an orange product, [$PdLCl_2$], in good yield [$^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = 192.34]. When reacted with [$Pt(NCMe)_2Cl_2$] in $CHCl_3$ under reflux, L gave a yellow product [$PtLCl_2$] [$^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 158.97 (s + d, 2P, $J_{P-195Pt}$ = 3924 Hz)].

¶ [$PdLCl_2$] and **1** were crystallized by slow evaporation at 0 °C in CH_2Cl_2–EtOH. All attempts to obtain crystals from other solvents failed. In a first crystallization, both compounds were present: red prisms of **1** (major) and fragile red needles of [$PdLCl_2$]. The latter crystals are not stable when removed from the mother liquor (loss of solvent); they decompose below 170 K and are partially transformed into **1** after a few hours.

The X-ray analysis of [$PdLCl_2$] (see above) was terminated before the end of the data collection due to decomposition of the crystal and it was not possible, despite numerous attempts, to obtain new crystals. Nevertheless, the resolution is sufficient and shows that the compound crystallizes with one CH_2Cl_2 and three EtOH guest molecules. Consequently, the crystals must be formed in the presence of EtOH and before the conversion of [$PdLCl_2$] into **1**. It is possible that the nucleophilic addition could take place within the crystal itself.

‖ The reaction of [$PdLCl_2$] in CH_2Cl_2 with an excess of MeOH or EtOH under reflux was periodically monitored by ^{31}P NMR. The reaction is complete, quantitatively, after 24 h and 5 days in MeOH and EtOH, respectively. The $^{31}P\{^1H\}$ NMR ($CDCl_3$) spectrum showed two doublets δ_{P1} 66.25, δ_{P2} 240.41 (d, J_{P1P2} 476 Hz) instead of a singlet. We have not succeeded in performing the same experiment with [$PtLCl_2$] because of the low stability of this compound in solution.

References

1 S. Chakladar, P. Paul, K. Venkatsubramanian and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1991, 2669; S. P. Molnar and M. Orchin, *J. Organomet. Chem.*, 1969, **16**, 196; H. Onoue and I. Moritani, *J. Organomet. Chem.*, 1972, **43**, 431; R. L. Bennett, M. I. Bruce, B. L. Goodall, M. Z. Iqbal and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1972, 1787.

2 Th. C. Klebach, R. Loureus and F. Bickelhaupt, *J. Am. Chem. Soc.*, 1978, **100**, 4886; Th. A. Van der Knaap and F. Bickelhaupt, *Tetrahedron Lett.*, 1982, **23**, 2037; R. de Vanmas, A. Marinetti and F. Mathey, *J. Organomet. Chem.*, 1991, **413**, 411.

3 A. Jouaiti, M. Geoffroy, G. Terron and G. Bernardinelli, *J. Chem. Soc., Chem. Commun.*, 1992, 155; A. Jouaiti, M. Geoffroy, G. Terron and G. Bernardinelli, *J. Am. Chem. Soc.*, 1995, **117**, 2251.

4 E. Blanc, D. Schwarzenbach and H. D. Flack *J. Appl. Crystallogr.*, 1991, **24**, 1035.

5 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq and M. M. Woolfson, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data, Universities of York and Louvain, 1987.

6 XTAL3.2 User's Manual, ed. S. R. Hall, H. D. Flack and J. M. Stewart, Universities of Western Australia and Maryland, 1992.

7 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

8 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

9 M. Camalli, F. Caruso, S. Chaloupka, E. M. Leber, H. Rimml and L. M. Venanzi, *Helv. Chim. Acta*, 1990, **73**, 2263.

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