Synthesis, Characterisation and Structure of Square-planar Palladium(II) Complexes with Phosphine–Pyridine Hybrid Ligands *o*-$Ph_2PC_6H_4CH_2O(CH_2)_nC_5H_4N$-2 (*n* = 1–3). Isolation of the First Transition-metal Complex with a *trans*-Chelating Bidentate PN Ligand†

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The reaction of $Na_2[PdCl_4]$ or $[PdCl_2(PhCN)_2]$ with an equimolar amount of new bidentate hybrid ligands having a P and a N donor atom capable of *trans* chelation, *o*-$Ph_2PC_6H_4CH_2O(CH_2)_nC_5H_4N$-2 (*n* = 1–3), gave mainly the 1 : 1 complex $[PdCl_2\{o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_nC_5H_4N\text{-}2\}]$. Depending on the length of the backbone connecting the phosphino and the pyridyl groups, *cis*- or *trans*-co-ordinated complexes were mainly formed; when *n* = 1 the *cis* complex **1** was formed, but the ligands with longer bridges gave the *trans* complexes **2** and **3** respectively as the main products. From the reaction of the palladium(II) complex with *o*-$Ph_2PC_6H_4CH_2O(CH_2)_nC_5H_4N$-2 (*n* = 2 or 3) the trinuclear complexes $[Pd_3Cl_6\{o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_nC_5H_4N\text{-}2\}_2]$ **4** (*n* = 2) and **5** (*n* = 3) were also obtained as minor products and the *cis*-chelated complexes analogous to **1** could not be isolated. The reaction of $Na_2[PdCl_4]$ with 2 equivalents of *o*-$Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N$-2 gave quantitatively the 1 : 2 complex *trans*-$[PdCl_2\{o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N\text{-}2\}_2]$ **7** in which the ligand is bound only through the P atom. This complex is in equilibrium with the *trans* 1 : 1 complex **3** in solution, dissociating one molecule of the ligand (K_{eq} = 5.6 × 10^{-3} mol dm^{-3}, 35 °C). On heating in CH_2Cl_2–tetrahydrofuran or diethyl ether, **3** partially isomerised to the dinuclear complex $[Pd_2Cl_4\{\mu\text{-}o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N\text{-}2\}_2]$ **6**, in which the hybrid ligands act as bridges. The crystal structures of **1**, **3** and **6** were determined; **3** is the first example of a transition-metal complex with a *trans*-spanning chelate phosphine–pyridine hybrid ligand. The reaction of the ligand *o*-$Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N$-2 with $K_2[PtCl_4]$, in contrast to the palladium complexes, always gave the 1 : 2 complex *trans*-$[PtCl_2\{o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N\text{-}2\}_2]$ **8** in good yield regardless of the ligand : Pt ratio. It did not dissociate in solution and the *trans*-chelated complex analogous to **3** could not be isolated even from the reaction of $K_2[PtCl_4]$ with an equimolar amount of the ligand *o*-$Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N$-2.

Bidentate phosphine–pyridine ligands, containing soft phosphorus and hard nitrogen donors are expected to exhibit unique catalytic activities. Thus, there is general interest in transition-metal complexes containing such hybrid ligands. Several complexes having these ligands have been prepared,[1] some of which are reported to be potential catalysts.[1c,e,f,i] All the complexes prepared so far are *cis*-chelated. Although there are a large number of square-planar complexes containing bidentate ligands, those with *trans*-chelating ligands are rare.[2] To our knowledge, there is only one example of a mononuclear complex containing *trans*-chelating bidentate hybrid ligands.[2g] In addition, almost all of the reported examples of transition-metal complexes with *trans*-chelating ligands lack an X-ray analysis. Such complexes are expected to show unique functions in catalysis.[3] The preparation of new complexes containing *trans*-chelating ligands and elucidation of their structures and properties is therefore of interest. Thus, we prepared new phosphine–pyridine hybrid ligands having bridges of different lengths, *o*-$Ph_2PC_6H_4CH_2O(CH_2)_nC_5H_4N$-2 (*n* = 1–3), capable of spanning the *trans* positions of square-planar complexes and investigated their reactions with palladium(II) complexes. Single-crystal X-ray diffraction analyses were also carried out. For the ligand *o*-$Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N$-2, the reaction with $K_2[PtCl_4]$ was investigated and found to be in sharp contrast with those of the palladium complexes. We have briefly reported the preparation and crystal structure of the complex *trans*-$[PdCl_2\{o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N\text{-}2\}]$.[4]

Experimental

All syntheses were carried out by using standard Schlenk techniques. The solvents were dried by standard methods and distilled under an inert gas atmosphere (N_2 or Ar) prior to use. Column chromatography was carried out with silica gel (Kieselgel, 230–400 mesh) as the stationary phase. Proton NMR spectra were obtained at 270.05 MHz on a JEOL GSX-270 spectrometer or at 399.65 MHz on a JEOL GSX-400 spectrometer, ^{31}P NMR spectra at 40.25 MHz on a JEOL FX-100 spectrometer or at 109.25 MHz on a JEOL GSX-270 spectrometer. Infrared spectra were obtained on a Hitachi 295 spectrophotometer, ultraviolet spectra on a Shimazu UV 265 FS recording spectrophotometer.

Materials.—2-(Diphenylphosphino)benzoic acid was prepared by the published procedure.[5] Pyridine-2-carbonyl chloride hydrochloride, 2-hydroxymethylpyridine, 2-(2-hydroxyethyl)pyridine and 2-(3-hydroxypropyl)pyridine were obtained fron Nacalai Tesque, and Aldrich Chemical. Silica gel was obtained from Merck.

Preparations.—*2-(Diphenylphosphino)benzyl alcohol.* To a stirred suspension of $LiAlH_4$ (2.5 g, 66 mmol) in tetrahydrofuran (thf) (90 cm^3) was added 2-(diphenylphosphino)benzoic acid

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(14.50 g, 47.3 mmol) under ice-cooling. The mixture was heated under reflux for 1 h then hydrolysed with aqueous NaOH (1 mol dm^{-3}, 20 cm^3) and the organic phase dried over $MgSO_4$. The solvent was removed *in vacuo* to give the alcohol as a pale yellow oil (14.4 g, 100%); δ_H($CDCl_3$, 270 MHz) 4.84 (2 H, d, J_{PH} 14.2 Hz, CH_2) and 6.89–7.65 (21 H, m, aromatic); ν(neat) 3350, 3048, 2900, 2850, 2805, 1582, 1480, 1430, 1015, 740 and 695 cm^{-1}. The alcohol could quantitatively be converted into the phosphine oxide by oxidation with 10% H_2O_2 in acetone under ice-cooling to give a colourless solid, m.p. 163–164 °C (from MeOH–water) (Found: C, 74.3; H, 5.7. $C_{19}H_{17}O_2P$ requires C, 74.0; H, 5.6%); δ_H($CDCl_3$, 270 MHz) 4.02 (1 H, br, OH), 4.58 (2 H, s, CH_2) and 6.99–7.67 (14 H, m, aromatic); ν(KBr tablet) 3320, 3045, 2900, 2850, 2810, 1725, 1588, 1480, 1435, 1320, 1245, 1165, 1115, 1100, 1080, 1050, 1000, 800, 760, 750, 720, 700 and 535 cm^{-1}.

o-(*Diphenylphosphoryl*)*benzyl bromide*. To a solution of 2-(diphenylphosphino)benzyl alcohol (6.28 g, 21.63 mmol) in chloroform (50 cm^3) was slowly added carbon tetrabromide (7.85 g, 22.9 mmol) and the mixture was stirred for 1 h. The solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel (ethyl acetate) to give the bromide as a white solid (7.95 g, 99%), m.p. 115–116 °C (Found: C, 61.6; H, 4.35; Br, 21.3. $C_{19}H_{16}BrOP$ requires C, 61.5; H, 4.3; Br, 21.5%); δ_H($CDCl_3$, 270 MHz) 5.02 (2 H, s, CH_2) and 7.0–7.7 (14 H, m, aromatic); ν(KBr tablet) 3030, 1585, 1560, 1470, 1430, 1230, 1190, 1115, 820, 760, 720, 700 and 690 cm^{-1}.

o-$Ph_2P(O)C_6H_4CH_2OCH_2C_5H_4N$-2. To a suspension of NaH (72 mg, 3.0 mmol) in thf (10 cm^3) was added 2-hydroxymethylpyridine (0.3 cm^3, 3.1 mmol) followed by a solution of *o*-(diphenylphosphoryl)benzyl bromide (1.00 g, 2.69 mmol) in thf (5 cm^3), and the mixture was stirred for 3 h at room temperature. It was filtered from the solid material, and the filtrate evaporated to dryness. The resulting crude oil was purified by column chromatography on silica gel (dichloromethane–ethanol, 9 : 1) to give the phosphine oxide as colourless crystals (0.91 g, 84%), m.p. 90 °C (Found: C, 75.05; H, 5.7; N, 3.5. $C_{25}H_{22}NO_2P$ requires C, 75.2; H, 5.55; N, 3.5%); δ_H($CDCl_3$, 270 MHz) 4.48 (2 H, s, $C_5H_4NCH_2O$), 4.98 (2 H, s, $C_6H_4CH_2O$), 7.0–7.8 (18 H, m, aromatic) and 8.48 (1 H, d, *J* 4.3 Hz, H^6 of C_5H_4N); δ_P($CHCl_3$–5% $CDCl_3$, 40.25 MHz) 31.85 (s); ν(KBr tablet) 3050, 2950, 2850, 1590, 1570, 1480, 1440, 1180, 1110, 755, 720 and 695 cm^{-1}.

o-$Ph_2P(O)C_6H_4CH_2O(CH_2)_2C_5H_4N$-2. This was prepared in the same way as above, from NaH (82 mg, 3.4 mmol), 2-(2-hydroxyethyl)pyridine (0.48 cm^3, 4.3 mmol), and *o*-(diphenylphosphoryl)benzyl bromide (1.06 g, 2.86 mmol), as colourless crystals (0.79 g, 67%), m.p. 99–101 °C (Found: C, 75.85; H, 6.0; N, 3.6. $C_{26}H_{24}NO_2P$ requires C, 75.3; H, 5.85; N, 3.4%); δ_H($CDCl_3$, 270 MHz) 2.90 (2 H, t, *J* 6.8, $C_5H_4NCH_2CH_2O$), 3.64 (2 H, t, *J* 6.6, $C_5H_4NCH_2CH_2O$), 4.98 (2 H, s, $C_6H_4CH_2O$), 7.0–7.8 (18 H, m, aromatic) and 8.48 (1 H, d, *J* 4.6 Hz, H^6 of C_5H_4N); δ_P($CHCl_3$–5% $CDCl_3$, 40.25 MHz) 31.83 (s); ν(KBr tablet) 3050, 2950, 2850, 1590, 1570, 1480, 1440, 1180, 1110, 755, 720 and 695 cm^{-1}.

o-$Ph_2P(O)C_6H_4CH_2O(CH_2)_3C_5H_4N$-2. This was similarly prepared from NaH (0.66 g, 27.5 mmol), 2-(3-hydroxypropyl)-pyridine (2.1 cm^3, 16.3 mmol), and *o*-(diphenylphosphoryl)-benzyl bromide (5.20 g, 14.0 mmol) as a yellow oil (5.25 g, 88%) (Found: C, 75.4; H, 6.2; N, 3.2%; $M + H^+$, 428.1779. $C_{27}H_{26}NO_2P$ requires C, 75.9; H, 6.1; N, 3.3%; $M + H^+$, 428.1779); δ_H($CDCl_3$, 270 MHz) 1.86 (2 H, m, $C_5H_4NCH_2CH_2CH_2O$), 2.76 (2 H, t, *J* 7.7, $C_5H_4NCH_2CH_2CH_2O$), 3.32 (2 H, t, *J* 6.3 Hz, $C_5H_4NCH_2CH_2CH_2O$), 4.80 (2 H, s, $C_6H_4CH_2O$), 6.78–7.56 (22 H, m, aromatic) and 8.50 (1 H, m, H^6 of C_5H_4N); δ_P($CHCl_3$–5% $CDCl_3$, 40.25 MHz) 32.02 (s); ν(neat) 3050, 2950, 2920, 2850, 1590, 1570, 1475, 1190, 1120, 750, 720, 710 and 695 cm^{-1}.

o-$Ph_2PC_6H_4CH_2OCH_2C_5H_4N$-2. To a stirred suspension of NaH (159 mg, 6.6 mmol) in thf (5 cm^3) was added a solution of 2-(diphenylphosphino)benzyl alcohol (970 mg, 3.32 mmol) in thf (10 cm^3), and the resulting mixture was heated under reflux overnight to yield a yellow suspension of sodium *o*-(diphenylphosphino)benzyl alcoholate, which was dropwise added to a solution of pyridine-2-carbonyl chloride (467 mg, 3.66 mmol) in thf (10 cm^3) at room temperature under argon. The reaction mixture was refluxed overnight, the solvent removed *in vacuo* and the residue purified by column chromatography on silica gel (dichloromethane–ethanol, 9 : 1) to give the hybrid ligand (1.14 g, 89%) as a colourless oil (Found: $M + H^+$, 384.1517. $C_{25}H_{22}NOP$ requires $M + H^+$, 384.1555); δ_H($CDCl_3$, 270 MHz) 4.59 (2 H, s, $C_5H_4NCH_2O$), 4.87 (2 H, d, J_{PH} 1.46, $C_6H_4CH_2O$), 6.91–7.61 (21 H, aromatic) and 8.48 (1 H, dt, *J* 0.7, 3.9 Hz, H^6 of C_5H_4N); δ_P($CDCl_3$–5% $CDCl_3$, 40.25 MHz) −15.31 (s); ν(neat) 3050, 3000, 2900, 2850, 1588, 1570, 1475, 1430, 1105, 1095, 750 and 695 cm^{-1}.

o-$Ph_2PC_6H_4CH_2O(CH_2)_2C_5H_4N$-2. To a Schlenk flask (100 cm^3) fitted with a condenser was added, under argon, a solution of *o*-$Ph_2P(O)C_6H_4CH_2O(CH_2)_2C_5H_4N$-2 (300 mg, 0.73 mmol) in MeCN (10 cm^3), NEt_3 (1.0 cm^3, 7.17 mmol) and $SiCl_3H$ (0.5 cm^3, 4.96 mmol) successively, and the mixture was refluxed for 30 min. After the flask was cooled in an ice-bath, 25% aqueous NaOH was added dropwise. The reaction mixture was filtered and the solvents removed to give a pale yellow oil. The crude products were purified by column chromatography on silica gel (dichloromethane–ethanol, 20 : 1) to give the hybrid ligand (280 mg, 97%) as a colourless oil (Found: $M + H^+$, 398.1674. $C_{26}H_{25}NOP$ requires $M + H^+$, 398.1644); δ_H($CDCl_3$, 270 MHz) 2.88 (2 H, t, *J* 6.9, $C_5H_4NCH_2CH_2O$), 3.76 (2 H, t, *J* 6.8, $C_5H_4NCH_2CH_2O$), 4.72 (2 H, d, J_{PH} 1.62, $C_6H_4CH_2O$), 6.85–7.54 (19 H, m, aromatic), 8.48 (1 H, d, *J* 2.4 Hz, H^6 of C_5H_4N); δ_P($CHCl_3$–5% $CDCl_3$, 40.25 MHz) −15.94 (s); ν(neat) 3050, 3000, 2900, 2850, 1590, 1567, 1430, 1090, 740 and 695 cm^{-1}.

o-$Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N$-2. This was prepared similarly by reduction of *o*-$Ph_2P(O)C_6H_4CH_2O(CH_2)_3C_5H_4N$-2 (300 mg, 0.70 mmol) with $SiCl_3H$ (0.5 cm^3, 4.96 mmol) and NEt_3 (1.0 cm^3, 7.17 mmol) as a colourless oil (280 mg, 97%) (Found: $M + H^+$, 412.1853. $C_{27}H_{26}NOP$ requires $M + H^+$, 412.1830); δ_H($CDCl_3$, 270 MHz) 1.88 (2 H, m, $C_5H_4NCH_2CH_2CH_2O$), 2.75 (2 H, t, *J* 7.7, $C_5H_4NCH_2CH_2CH_2O$), 3.44 (2 H, t, *J* 6.3, $C_5H_4NCH_2CH_2CH_2O$), 4.69 (2 H, d, $C_6H_4CH_2O$, J_{PH} 0.8 Hz), 6.87–7.56 (22 H, m, aromatic), 8.49 (1 H, m, H^6 of C_5H_4N); δ_P($CHCl_3$–5% $CDCl_3$, 40.25 MHz) −15.96 (s); ν(neat) 3050, 3000, 2900, 2850, 1590, 1565, 1475, 1430, 1095, 740 and 695 cm^{-1}.

Reaction of $Na_2[PdCl_4]$ *with* *o*-$Ph_2PC_6H_4CH_2OCH_2C_5H_4N$-2. To a solution of $Na_2[PdCl_4]$ (355 mg, 1.21 mmol) in a mixture of ethanol (3 cm^3) and degassed water (4 cm^3) was added dropwise a solution of *o*-$Ph_2PC_6H_4CH_2OCH_2C_5H_4N$-2 (467 mg, 1.22 mmol) in ethanol (5 cm^3). The reaction mixture was stirred for 1 h at room temperature to give a yellow suspension. The yellow crystalline solid was filtered off, washed with hexanes, and dried in air (608 mg). Its ^1H NMR spectrum indicated the presence of the two isomeric products, *cis*-[$PdCl_2$(*o*-$Ph_2PC_6H_4CH_2OCH_2C_5H_4N$-2] **1** and *trans*-[$PdCl_2$(*o*-$Ph_2PC_6H_4CH_2OCH_2C_5H_4N$-2)] in 4 : 1 ratio. Careful recrystallisation from dichloromethane or dichloromethane–ethanol gave an analytically pure sample of **1** as yellow crystals, m.p. 223–224 °C (decomp.) (Found: C, 50.8; H, 3.85; Cl, 17.55; N, 2.4. $C_{25}H_{22}Cl_2NOPPd \cdot 0.5CH_2Cl_2$ requires C, 50.8; H, 3.8; Cl, 17.6; N, 2.3%); δ_H(CD_2Cl_2, 270 MHz) 4.45 (1 H, d, J_{gem} 13.5, $C_5H_4NCH_2O$), 4.53 (1 H, d, J_{gem} 12.4, $C_6H_4CH_2O$), 4.98 (1 H, br, $C_5H_4NCH_2O$), 5.61 (1 H, d, J_{gem} 12.4, $C_6H_4CH_2O$), 6.81–8.17 (18 H, m, aromatic) and 8.88 (1 H, d, *J* 5.0 Hz, H^6 of C_5H_4N); δ_P(CD_2Cl_2, 109.25 MHz) 23.23 (s); ν(Nujol mull) 3050, 1603, 1570, 1100, 1085, 750, 690, 335 and 285 cm^{-1}; λ_{max}/nm (CH_2Cl_2, log ε) 276 (4.16) and 361 (3.34).

The *trans* isomer could not be isolated in pure form but its formation in the crude product was suggested from the NMR spectra: δ_H($CDCl_3$, 270 MHz) 5.51 (2 H, s, $C_5H_4NCH_2O$), 5.54 (2 H, s, $C_6H_4CH_2O$), 6.85–8.05 (18 H, aromatic) and 8.74 (1 H, m, H^6 of C_5H_4N); δ_P($CDCl_3$–5% $CDCl_3$, 40.25 MHz) 24.41 (s).

Reaction of $[PdCl_2(PhCN)_2]$ *with* *o*-$Ph_2PC_6H_4CH_2$-

$OCH_2C_5H_4N$-2. From the reaction of $[PdCl_2(PhCN)_2]$ (76 mg, 0.20 mmol) and *o*-$Ph_2PC_6H_4CH_2OCH_2C_5H_4N$-2 (76 mg, 0.20 mmol) in dichloromethane (20 cm^3) a similar yellow solid mixture comprised of complex **1** and the *trans* isomer was obtained in about 70% yield.

Reaction of $Na_2[PdCl_4]$ *with* *o*-$Ph_2PC_6H_4CH_2O(CH_2)_2C_5H_4N$-2. To a brown suspension of $Na_2[PdCl_4]$ (194 mg, 0.66 mmol) in ethanol (5 cm^3) was added dropwise a solution of *o*-$Ph_2PC_6H_4CH_2O(CH_2)_2C_5H_4N$-2 (263 mg, 0.66 mmol) in ethanol (5 cm^3). The mixture was stirred for 1 h at room temperature to give a yellow suspension, the solvent was removed *in vacuo*, and the residue dissolved in dichloromethane (5 cm^3). Addition of the filtered dichloromethane solution to ethanol (20 cm^3) gave a yellowish orange precipitate (360 mg), which contains two compounds, $[Pd_3Cl_6\{o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_2C_5H_4N\text{-}2\}_2]$ **4** and *trans*-$[PdCl_2\{o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_2C_5H_4N\text{-}2\}]$ **2**, the former predominating. Careful and repeated recrystallisation from dichloromethane–ethanol afforded **4** (160 mg) as yellow needles from the less soluble part and **2** (172 mg) as orange prisms from the more soluble part. Complex **4**: m.p. 208–209.5 °C (Found: C, 46.5; H, 3.9; Cl, 16.2; N, 2.1. $C_{52}H_{48}Cl_6N_2O_2P_2Pd_3$ requires C, 47.1; H, 3.65; Cl, 16.0; N, 2.1%); $\delta_H(CDCl_3$, 270 MHz) 3.97 (2 H, t, *J* 6.6, $C_5H_4NCH_2CH_2O$), 4.41 (2 H, t, *J* 6.4, $C_5H_4NCH_2CH_2O$), 5.25 (2 H, s, $C_6H_4CH_2O$), 6.93–7.85 (21 H, m, aromatic) and 8.98 (1 H, dd, *J* 6.4, 1.6 Hz, H^6 of C_5H_4N); $\delta_P(CHCl_3$–5% $CDCl_3$, 40.25 MHz) 17.03 (s); ν(Nujol mull) 3050, 1603, 1570, 1100, 772, 753, 744, 690, 350, 305 and 265 cm^{-1}; λ_{max}/nm (CH_2Cl_2, log ε) 270 (sh) (4.20) and 351 (4.41). Complex **2**: m.p. 210 °C (decomp.) (Found: C, 52.0; H, 4.2; Cl, 14.9; N, 2.0. $C_{26}H_{24}Cl_2NOPPd\cdot 0.25CH_2Cl_2$ requires C, 52.9; H, 4.1; Cl, 14.9; N, 2.35%); $\delta_H(CDCl_3$, 270 MHz) 3.87 (2 H, t, *J* 11.8, $C_5H_4NCH_2CH_2O$), 4.49 (2 H, t, *J* 7.7 Hz, $C_5H_4NCH_2CH_2O$), 5.64 (2 H, s, $C_6H_4CH_2O$), 6.92–7.92 (23 H, m, aromatic) and 8.81 (1 H, m, H^6 of C_5H_4N); $\delta_P(CDCl_3$–5% $CDCl_3$, 40.25 MHz) 23.13 (s); ν(Nujol mull) 3050, 1670, 1603, 1100, 765, 740, 705, 690 and 350 cm^{-1}; λ_{max}/nm (CH_2Cl_2, log ε) 265 (sh) (3.97), 273 (3.99), 290 (4.02) and 360 (3.00).

Reaction of $[PdCl_2(PhCN)_2]$ *with* *o*-$Ph_2PC_6H_4CH_2O(CH_2)_2C_5H_4N$-2. Reaction of $[PdCl_2(PhCN)_2]$ (139 mg, 0.42 mmol) and *o*-$Ph_2PC_6H_4CH_2O(CH_2)_2C_5H_4N$-2 (144 mg, 0.42 mmol) in dichloromethane (15 cm^3) also gave a yellow-orange solid (229 mg) containing complexes **4** and **2** in 1:2 ratio.

Reaction of $Na_2[PdCl_4]$ *with* *o*-$Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N$-2. To a suspension of $Na_2[PdCl_4]$ (310 mg, 1.05 mmol) in ethanol (5 cm^3) was added dropwise a solution of *o*-$Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N$-2 (438 mg, 1.06 mmol) in ethanol (5 cm^3). The reaction mixture was stirred for 1 d at room temperature to give a yellowish orange suspension, the solvent was removed *in vacuo* and the residue dissolved in dichloromethane (8 cm^3). The suspension was filtered and the filtrate evaporated *in vacuo* to give a yellow-orange solid. Recrystallisation of this from dichloromethane–hexanes gave yellow needles of $[Pd_3Cl_6\{o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N\text{-}2\}_2]$ **5** (227 mg). An orange prism of *trans*-$[PdCl_2\{o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N\text{-}2\}]$ **3** (334 mg) was isolated from the mother-liquor by recrystallisation from dichloromethane–hexanes. Complex **5**: m.p. 196–197 °C (decomp.) (Found: C, 47.6; H, 3.9; Cl, 15.15; N, 2.1. $C_{54}H_{52}Cl_6N_2O_2P_2Pd_3$ requires C, 47.8; H, 3.9; Cl, 15.7; N, 2.1%); $\delta_H(CDCl_3$, 270 MHz) 2.30 (2 H, dt, *J* 6.2, 16.9, $C_5H_4NCH_2CH_2CH_2O$), 3.96 (2 H, t, *J* 6.2, $C_5H_4NCH_2CH_2CH_2O$), 4.04 (2 H, t, *J* 8.1, $C_5H_4NCH_2CH_2CH_2O$), 5.60 (2 H, s, $C_6H_4CH_2O$), 6.89–7.95 (23 H, m, aromatic) and 9.04 (1 H, ddd, *J* 2.8, 0.7, 0.4 Hz, H^6 of C_5H_4N); $\delta_P(CDCl_3$, 109.25 MHz) 27.41 (s); ν(Nujol mull) 3050, 1603, 1570, 1090, 760, 745, 730, 690, 355, 305 and 265 cm^{-1}; λ_{max}/nm (CH_2Cl_2, log ε) 265 (sh) (4.00), 273 (sh) (3.94), 311 (4.28) and 392 (3.76). Complex **3**: m.p. 213–214.5 °C (decomp.) (Found: C, 49.95; H, 4.3; Cl, 20.7; N, 2.1. $C_{27}H_{26}Cl_2NOPPd\cdot CH_2Cl_2$ requires C, 49.9; H, 4.2; Cl, 21.05; N, 2.1%); $\delta_H(CDCl_3$, 270 MHz) 2.59 (2 H, dt, *J* 8.0, 5.9, $C_5H_4NCH_2CH_2CH_2O$), 3.53 (2 H, m, $C_5H_4NCH_2CH_2CH_2O$), 3.98 (2 H, t, *J* 5.7 Hz, $C_5H_4NCH_2CH_2CH_2O$), 5.59 (2 H, s, $C_6H_4CH_2O$), 6.86–7.95 (21 H, m, aromatic) and 8.90 (1 H, m, H^6 of C_5H_4N); $\delta_P(CDCl_3$, 109.25 MHz) 23.41 (s); ν(Nujol mull) 1603, 1570, 1090, 765, 753, 710, 690, 350(sh) and 343 cm^{-1}; λ_{max}/nm (CH_2Cl_2, log ε) 267 (sh) (3.95), 277 (sh) (4.09), 290 (4.14) and 365 (3.08).

Reaction of $[PdCl_2(PhCN)_2]$ *with* *o*-$Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N$-2. Reaction of $[PdCl_2(PhCN)_2]$ (132 mg, 0.35 mmol) and *o*-$Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N$-2 (142 mg, 0.35 mmol) in dichloromethane (15 cm^3) also gave a yellow-orange solid (229 mg) containing complexes **5** and **3** in 1:6 ratio.

$[Pd_2Cl_4\{\mu\text{-}o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N\text{-}2\}_2]$ **6**. In a Schlenk flask complex **3** (35 mg, 0.06 mmol) was dissolved in a mixture of CH_2Cl_2 (3 cm^3) and thf (3 cm^3). The flask was sealed with a glass stopper and the reaction mixture stirred at 65 °C for 10 h. The solvents were removed *in vacuo* to give an orange solid comprised of the starting complex **3** and **6**. Recrystallisation from dichloromethane–Et_2O afforded the dinuclear complex **6** as larger orange prisms (14 mg, 40%) which could be separated mechanically from orange prisms of **3**. Complex **6**: m.p. 225–227 °C (decomp.) (Found: C, 53.5; H, 4.4; Cl, 13.35; N, 2.3. $C_{54}H_{52}Cl_4N_2O_2P_2Pd_2$ requires C, 55.1; H, 4.45; Cl, 12.0; N, 2.4%); $\delta_H(CDCl_3$, 270 MHz) 2.22 (2 H, m, $C_5H_4NCH_2CH_2CH_2O$), 3.53 (2 H, m, $C_5H_4NCH_2CH_2CH_2O$), 3.72 (2 H, m, $C_5H_4NCH_2CH_2CH_2O$), 5.22 (2 H, d, *J* 1.4 Hz, $C_6H_4CH_2O$), 6.86–7.95 (21 H, m, aromatic) and 8.82 (1 H, m, H^6 of C_5H_4N); $\delta_P(CDCl_3$, 109.25 MHz) 23.85 (s); ν(Nujol mull) 3050, 1603, 1570, 1090, 765, 753, 710, 690 and 343 cm^{-1}.

trans-$[PdCl_2\{o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N\text{-}2\}_2]$ **7**. To a solution of *o*-$Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N$-2 (360 mg, 0.87 mmol) in ethanol (5 cm^3) was added a solution of $Na_2[PdCl_4]$ (85 mg, 0.29 mmol) in water (5 cm^3). The reaction mixture was stirred for 1 h to give a yellow suspension. The suspension was filtered and the solid was washed with water then diethyl ether to give complex **7** as yellow needles (252 mg, 87%), m.p. 189–190 °C (decomp.) (Found: C, 64.4; H, 5.3; Cl, 6.8; N, 2.9. $C_{54}H_{52}Cl_2N_2O_2P_2Pd_2$ requires C, 64.8; H, 5.2; Cl, 7.1; N, 2.8%). The ^1H NMR spectrum showed signals due to the free ligand *o*-$Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N$-2 and **3** besides those of **7**: $\delta_H(CDCl_3$, 270 MHz) 1.90 (4 H, m, $C_5H_4NCH_2CH_2CH_2O$), 2.76 (4 H, m, $C_5H_4NCH_2CH_2CH_2O$), 3.37 (4 H, m, $C_5H_4NCH_2CH_2CH_2O$), 5.07 (4 H, s, $C_6H_4CH_2O$), 6.87–7.81 (34 H, m, aromatic) and 8.50 (2 H, m, H^6 of C_5H_4N); $\delta_P(CDCl_3$, 109.25 MHz) 17.57 (s); ν(KBr tablet) 3050, 2900, 2850, 1590, 1570, 1480, 1430, 1095, 750, 695, 510 and 355 cm^{-1}.

trans-$[PtCl_2\{o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N\text{-}2\}_2]$ **8**. To a solution of *o*-$Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N$-2 (300 mg, 0.73 mmol) in ethanol (10 cm^3) was added a solution of $K_2[PtCl_4]$ (100 mg, 0.24 mmol) in water (5 cm^3). The reaction mixture was stirred for 1 h to give a lemon coloured suspension. The suspension was filtered and the solid was washed with water then diethyl ether to give complex **8** as lemon needles (263 mg, 100%), m.p. 189–190 °C (decomp.) (Found: C, 59.1; H, 4.9; Cl, 6.5; N, 2.5. $C_{54}H_{52}Cl_2N_2O_2P_2Pt_2$ requires C, 59.6; H, 4.8; Cl, 6.5; N, 2.6%); $\delta_H(CDCl_3$, 270 MHz) 1.90 (4 H, m, $C_5H_4NCH_2CH_2CH_2O$), 2.78 (4 H, t, *J* 7.7, $C_5H_4NCH_2CH_2CH_2O$), 3.35 (4 H, t, *J* 6.3 Hz, $C_5H_4NCH_2CH_2CH_2O$), 5.05 (4 H, s, $C_6H_4CH_2O$), 6.95–7.84 (34 H, m, aromatic) and 8.50 (2 H, m, H^6 of C_5H_4N); $\delta_P(CDCl_3$, 109.25 MHz) 14.65 (s with a pair of satellites, J_{PtP} 2596 Hz); ν(Nujol mull) 3050, 1593, 1565, 1480, 1435, 1100, 750, 695, 515, 505, 470 and 342 cm^{-1}.

Crystallographic Analyses.—Crystals of complexes **1** and **6** suitable for X-ray measurements were grown from a mixed solvent (CH_2Cl_2–Et_2O) by slow evaporation at ambient temperature. A crystal of **3** was obtained from CH_2Cl_2–hexanes at ambient temperature. The crystals of **1** and **3** were fixed at the end of a glass fibre with epoxy resin. That of **6** was placed in a thin-walled glass capillary with silicon grease and then flame sealed. All measurements were done using a Rigaku AFC-4R or

Table 1 Crystallographic data for the complexes

	1	3	6
Formula	$C_{25}H_{22}Cl_2NOPPd\cdot0.5CH_2Cl_2$	$C_{27}H_{26}Cl_2NOPPd\cdot CH_2Cl_2$	$C_{54}H_{52}Cl_4N_2O_2P_2Pd_2$
Colour	Yellow	Orange	Orange
M	603.22	673.73	1177.62
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
a/Å	12.867(1)	10.135(1)	10.698(1)
b/Å	11.224(1)	16.171(2)	15.453(3)
c/Å	17.560(2)	9.023(1)	15.311(3)
α/°		99.98(1)	
β/°	103.856(8)	101.41(1)	92.69(1)
γ/°		86.51(1)	
U/Å^3	2462.2(4)	1427.0(2)	2528.8(8)
Z	4	2	2
D_c/g cm^{-3}	1.627	1.568	1.547
D_m/g cm^{-3}	1.605(2)	1.54(2)	1.516(10)
F(000)	1212	680	1192
Crystal size/mm	0.30 × 0.20 × 0.15	0.20 × 0.25 × 0.25	0.43 × 0.37 × 0.02
λ/Å	0.710 69 (Mo-Kα, 9 kW)	0.710 69 (Mo-Kα, 8 kW)	0.710 69 (Mo-Kα, 8 kW)
T/K	298 ± 1	293 ± 1	293 ± 1
Scan mode	2θ–ω	2θ–ω	2θ–ω
$2\theta_{max}$/°	55.0	60.0	60.0
Collection region	$\pm h + k + l$	$\pm h + k \pm l$	$+h + k \pm l$
No. of measured reflections	5945	8600	7729
No. of unique reflections	5689	8324	7373
R_{sym} on F_o	0.020	0.022	0.014
No. of observed reflections	3827 [> 5.0σ(F_o)]	4789 [> 6.0σ(F_o)]	5371 [> 5.0σ(F_o)]
μ/cm^{-1}	11.55	10.97	10.19
Correction factors[a]	0.9924–1.0730	0.9871–1.1018	1.0002–1.0405
Variable parameters	373	325	298
R, R'	0.0396, 0.0293	0.0338, 0.0401	0.0295, 0.0369
Goodness of fit[b]	1.576	1.252	1.440
Maximum, minimum Δρ[c]/e Å^{-3}	0.54, −0.66	0.52, −0.46	0.56, −0.46
Maximum, average Δ/σ[d]	0.000, 0.000	0.002, 0.000	0.007, 0.000

[a] Relative absorption correction coefficient. Correction methods applied were those in ref. 6. [b] $[\Sigma w(F_o - F_c)^2/(N_o - N_p)]^{\frac{1}{2}}$, where N_o, N_p = number of observations and parameters. [c] Residual electron density on final Fourier-difference map. [d] In the final refinement cycle.

AFC-5R diffractometer equipped with a Rotaflex rotating-anode X-ray generator and a graphite monochromator. No significant decomposition of any crystal occurred during the respective data collections. Lorentz and polarisation corrections were applied for each structure. An empirical absorption correction was applied using transmission data.[6] Each structure was solved by a combination of the direct method (SHELXS 86),[7] a Fourier and a Fourier-difference technique and refined by a full-matrix least-squares method (ANYBLK).[8] The function minimised was $\Sigma_{hkl}w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. Neutral-atom scattering factors and anomalous dispersion terms were taken from ref. 9.

Compound **1**. Non-hydrogen atoms of complex **1** were anisotropically refined. Carbon and chlorine atoms of the CH_2Cl_2 solvate molecule were easily found and located near the centre of symmetry in a Fourier-difference map. The occupancy factor of the solvent atoms was 0.5 and these atoms were anisotropically refined. In the final refinement cycle, atomic coordinates of the hydrogen atoms were refined and their thermal parameters were fixed contributions. Hydrogen atoms of the solvate molecule, however, were not included in the calculations.

Compounds **3** *and* **6**. The final cycle of the full-matrix least-squares refinement used anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms were included at idealized positions and not refined in the final refinement cycle.

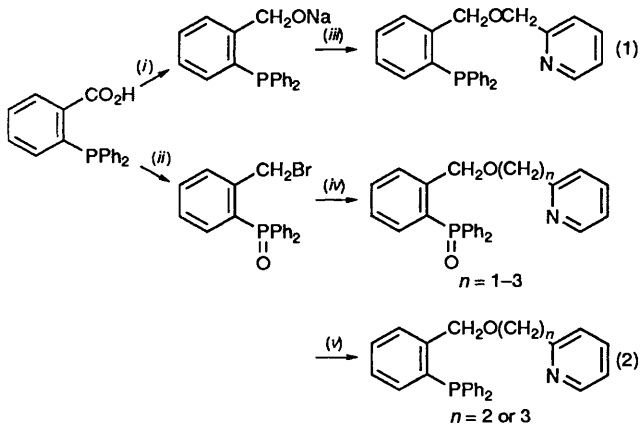
All calculations were performed on a NEC ACOS 930S computer at the Research Centre for Protein Engineering, Institute for Protein Research, Osaka University. For a summary of the crystal data and refinement details see Table 1. Fractional coordinates are listed in Tables 2–4, and the molecular structures with numbering scheme were drawn with the ORTEP II program[10] using 50% probability ellipsoids.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Preparation of Ligands.—As phosphine–pyridine hybrid ligands which are able to span the *trans* positions of square-planar complexes we designed the ligands *o*-$Ph_2PC_6H_4CH_2O$-$(CH_2)_nC_5H_4N$-2 (n = 1–3) which have a backbone of various lengths connecting a tertiary phosphine and a pyridine. The backbone is constructed from an *o*-phenylene group enforcing the *trans* co-ordination and an oxomethylene chain adjusting the distance between the co-ordinating groups. The ligand *o*-$Ph_2PC_6H_4CH_2OCH_2C_5H_4N$-2 was prepared from *o*-diphenylphosphinobenzoic acid according to equation (1), Scheme 1. The ligands *o*-$Ph_2PC_6H_4CH_2O(CH_2)_nC_5H_4N$-2 ($n$ = 2 or 3) were prepared according to equation (2), Scheme 1. Preparation of *o*-$Ph_2PC_6H_4CH_2OCH_2C_5H_4N$-2 according to equation (2) was unsuccessful because reduction of the corresponding phosphine oxide with trichlorosilane and triethylamine produced a lot of by-products due to cleavage of the benzylic ether linkage during the reduction. The reason for this different behaviour between the phosphine oxides is not clear. All the hybrid ligands are air-sensitive colourless oils, easily oxidised to the corresponding phosphine oxides. Thus, the purification of the reaction products was accomplished by rapid chromatography on silica gel under an inert-gas atmosphere.

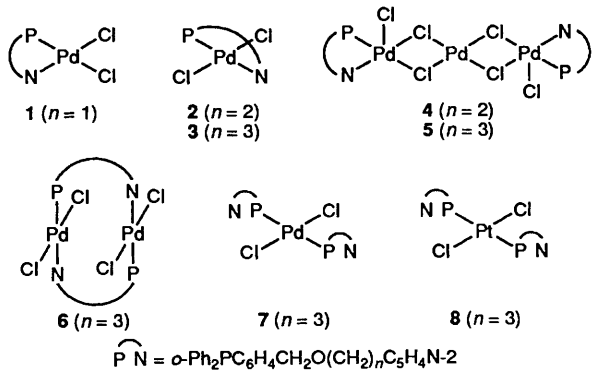
Reaction of $Na_2[PdCl_4]$ *or* $[PdCl_2(PhCN)_2]$ *with the Hybrid Ligands*.—Reaction of *o*-$Ph_2PC_6H_4CH_2OCH_2C_5H_4N$-2 and an equimolar amount of $Na_2[PdCl_4]$ in aqueous ethanol or



Scheme 1 (*i*) (*a*) $LiAlH_4$, (*b*) NaH; (*ii*) (*a*) $LiAlH_4$, (*b*) CBr_4; (*iii*) 2-$(ClCH_2)C_5H_4N$; (*iv*) $NaO(CH_2)_nC_5H_4N$-2; (*v*) $SiCl_3H$–NEt_3

$[PdCl_2(PhCN)_2]$ in dichloromethane gave yellow crystals of *cis*-$[PdCl_2\{o\text{-}Ph_2PC_6H_4CH_2OCH_2C_5H_4N\text{-}2\}]$ **1** as the main product after careful recrystallisation of the crude product from dichloromethane or dichloromethane–ethanol. The bidentate co-ordination of the ligand in **1** was suggested by the observation of ν(py CN) at 1603 cm^{-1} in the IR spectrum (Nujol mull), a shift of *ca.* 15 cm^{-1} from that of the free ligand (1588 cm^{-1}).[1b] Also the ^{31}P NMR spectrum consisted of a singlet at δ 23.23, shifted by 38.54 ppm from that of the free ligand (δ −15.31). The doublet signal due to H^6 of the pyridine ring at δ 8.88 was shifted by *ca.* 0.40 ppm from that of the free ligand (δ 8.48). The crude product contained the *trans* isomer analogous to complexes **2** and **3** as a minor component, which could not be obtained in a pure form. This geometry was suggested by the appearance of the characteristic signal at δ 8.74 due to H^6 of the pyridine ring co-ordinated in the *trans* position to phosphorus (see below). Well formed crystals of complex **1** were obtained and X-ray single-crystal analysis confirmed the structure to involve a *cis*-chelated square-planar complex. Consistently the IR spectrum showed two broad Pd–Cl stretching bands at 335 and 285 cm^{-1}. The ratio of the *cis* and *trans* complexes in the crude product was about 1 : 0.2.

Reaction of *o*-$Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N$-2 and an equimolar amount of $Na_2[PdCl_4]$ in absolute ethanol or $[PdCl_2(PhCN)_2]$ in dichloromethane gave *trans*-$[PdCl_2\{o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N\text{-}2\}]$ **3** as orange crystals in about 40% yield. As a minor by-product the trinuclear complex $[Pd_3Cl_6\{o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N\text{-}2\}_2]$ **5** was isolated as yellow crystals. Neither the *cis*-chelated mononuclear complex analogous to **1** nor the binuclear one **6** (see below) having a bridging hybrid ligand was detected in the reaction mixture. Separation between these two products could be achieved by the solubility difference, **3** being more soluble than **5** in common organic solvents. The ratio of **3** and **5** in the crude reaction mixture was about 6 : 1. When the reaction was conducted in aqueous ethanol, just as with $Ph_2PC_6H_4CH_2OCH_2C_5H_4N$-2, a very complicated mixture formed. Single crystals of **3** suitable for X-ray analysis were obtained by recrystallisation from dichloromethane–diethyl ether and the X-ray structural analysis clearly established the *trans* chelation of the ligand. The spectroscopic data for **3** indicated that the ligand acts in a bidentate manner and that the *trans*-square-planar structure persists also in solution; with the observation of ν(py CN) at 1603 cm^{-1}, a shift of *ca.* 13 cm^{-1} from that of the free ligand (1590 cm^{-1}), and δ_P 23.41, a shift of 39.37 ppm from that of the free ligand (δ_P −15.96). The signal of H^6 of the pyridine ring occurred at δ 8.90, a shift of 0.41 ppm compared with that of the free ligand (δ 8.49); the signal shape with a complex fine structure is very characteristic and is probably due to coupling with the *trans*-phosphorus atom. The corresponding



signal of the *cis* complex **1** appears as a doublet as mentioned above. The Pd–Cl stretching frequency occured as a fairly sharp main band at 343 cm^{-1} accompanied by a shoulder at 350 cm^{-1}. The observation of a band with a shoulder instead of a single band[11] does not preclude a *trans* structure for square-planar MX_2L_2 with non-centrosymmetric complexes.[2g,12]

The elemental analyses of the yellow crystals **5** indicated that the complex has a molecular formula $Pd_3Cl_6L_2$ [L = *o*-$Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N$-2]. The FAB mass spectrum also supported the trinuclear structure, showing a multiline signal due to the presence of isotopes of palladium and chlorine, with maximum at *m*/*z* 1323 due to the ion $M^+ - Cl$. A computer simulation for $Pd_3Cl_5L_2$ showed a similar multiline signal having a maximum at *m*/*z* 1320. The deviation of the experimental result from the calculated value is probably due to the abstraction of several protons from the complex ion. The ^1H and ^{31}P NMR spectra indicate that the two ligands are magnetically equivalent. The lower-field shift of the H^6 signal of the pyridine ring compared to that of the free ligand in the ^1H NMR (δ_H 9.04 *vs.* 8.49) and the singlet signal in ^{31}P-$\{^1H\}$ NMR spectrum (δ_P 27.41 *vs.* −15.96 for the free ligand) indicated unambiguously that the ligand is co-ordinated to the palladium through P and N. The appearance of the C=N stretching of the pyridine ring at a higher wavenumber compared to that of the free ligand (1603 *vs.* 1590 cm^{-1}) also indicates co-ordination through the pyridyl nitrogen. Complex **5** showed three bands at 355, 305 and 265 cm^{-1} in the region of ν(Pd–Cl) vibrations. That at 355 cm^{-1} could be assigned to the terminal Pd–Cl stretching and those at 305 and 265 cm^{-1} to the bridging Pd–Cl stretching.[13] Complex **5** was a non-conductor in solution. The results show that it is a neutral trinuclear complex having a $Pd(\mu\text{-}Cl)_2Pd(\mu\text{-}Cl)_2Pd$ unit, each palladium at both ends bearing a terminal chloride and a bidentate ligand; the yellow colour indicates the absence of Pd–Pd bonding. A similar trinuclear palladium core has been reported in $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)_2Pd(\mu\text{-}Cl)_2Pd(\eta^3\text{-}C_3H_5)]$.[14] As single crystals of complex **5** suitable for X-ray analysis were not obtained, its structure could not be established unambiguously. When the ligand was employed in excess in the above reaction, **3** was always contaminated with the 1 : 2 complex $[PdCl_2\{o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N\text{-}2\}_2]$ **7** (see below) and the separation between these two complexes was difficult.

The reaction with the ligand *o*-$Ph_2PC_6H_4CH_2O(CH_2)_2C_5H_4N$-2 gave a similar result: namely the *trans*-co-ordinated 1 : 1 complex *trans*-$[PdCl_2\{o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_2C_5H_4N\text{-}2\}]$ **2** and the trinuclear complex $[Pd_3Cl_6\{o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_2C_5H_4N\text{-}2\}_2]$ **4** were obtained in about 2 : 1 ratio. Complex **2** shows analytical and spectroscopic data analogous to those of **3** (see Experimental section) and thus it is concluded that it has a similar mononuclear *trans* structure. Elemental analyses of **4** support the molecular formula given and the ^1H NMR and IR spectra are also similar to those of **5**, but the electronic spectrum is different. The ^{31}P NMR spectrum showed a singlet signal at δ 17.03, a shift of *ca.* 10.4 ppm compared to that of **5**. The FAB mass spectrum showed a

Table 2 Fractional atomic coordinates ($\times 10^4$) with estimated standard deviations (e.s.d.s) in parentheses for complex **1**

Atom	*x*	*y*	*z*
Pd	127.4(3)	420.4(3)	1648.6(2)
Cl(1)	1204(1)	1655(1)	1074(1)
Cl(2)	−987(1)	1966(1)	1744(1)
P	−921(1)	−811(1)	2152(1)
O	1268(2)	−748(3)	3180(2)
N	1125(3)	−923(3)	1487(2)
C(1)	−466(3)	−2367(4)	2228(2)
C(2)	−1048(4)	−3204(5)	1719(3)
C(3)	−740(4)	−4392(5)	1763(3)
C(4)	168(5)	−4733(4)	2306(3)
C(5)	753(4)	−3911(5)	2811(3)
C(6)	454(3)	−2720(4)	2794(2)
C(7)	1084(4)	−1922(5)	3428(3)
C(8)	2159(4)	−680(4)	2835(3)
C(9)	1982(3)	−1255(4)	2044(2)
C(10)	2699(4)	−2077(4)	1880(3)
C(11)	2544(5)	−2541(5)	1140(3)
C(12)	1665(5)	−2199(5)	572(3)
C(13)	969(4)	−1395(5)	764(3)
C(14)	−2234(3)	−856(4)	1480(2)
C(15)	−3166(4)	−1056(5)	1718(3)
C(16)	−4126(4)	−1148(6)	1163(4)
C(17)	−4171(5)	−1081(5)	384(4)
C(18)	−3253(6)	−859(6)	138(3)
C(19)	−2292(4)	−761(5)	686(3)
C(20)	−1147(3)	−536(4)	3119(2)
C(21)	−1520(4)	−1471(5)	3501(3)
C(22)	−1674(4)	−1311(5)	4248(3)
C(23)	−1470(4)	−233(6)	4612(3)
C(24)	−1114(5)	690(5)	4235(3)
C(25)	−946(4)	552(5)	3487(3)

Table 3 Fractional atomic coordinates ($\times 10^5$) with e.s.d.s in parentheses for complex **3**

Atom	*x*	*y*	*z*
Pd	23 972(3)	68 651(2)	25 539(4)
Cl(1)	41 548(11)	73 110(7)	16 646(12)
Cl(2)	7 711(12)	63 646(8)	36 074(14)
P	17 422(10)	81 712(6)	35 390(10)
N	28 627(38)	56 363(24)	15 478(43)
O	−6 003(32)	72 595(27)	−9 426(37)
C(1)	−797(37)	82 900(25)	29 618(44)
C(2)	−8 874(43)	85 074(28)	40 834(50)
C(3)	−22 751(49)	85 695(33)	36 354(64)
C(4)	−28 665(45)	84 002(32)	21 013(67)
C(5)	−20 906(43)	81 889(30)	10 130(54)
C(6)	−6 867(39)	81 283(26)	14 140(46)
C(7)	1 086(43)	78 816(31)	1 301(47)
C(8)	1 360(56)	68 763(43)	−21 245(54)
C(9)	13 356(52)	63 309(37)	−15 062(52)
C(10)	9 438(52)	57 048(37)	−5 788(56)
C(11)	21 320(51)	52 475(30)	2 244(53)
C(12)	24 913(68)	44 275(40)	−3 512(74)
C(13)	36 063(80)	40 320(39)	3 858(90)
C(14)	43 564(65)	44 486(39)	16 935(82)
C(15)	39 345(54)	52 527(33)	22 560(61)
C(16)	23 887(37)	90 897(24)	30 085(38)
C(17)	37 780(41)	92 123(27)	33 706(42)
C(18)	43 006(45)	99 168(30)	30 304(47)
C(19)	34 713(53)	105 028(30)	23 657(52)
C(20)	20 928(53)	103 985(31)	20 275(55)
C(21)	15 536(44)	96 919(29)	23 491(47)
C(22)	22 096(39)	83 965(25)	56 209(39)
C(23)	29 251(46)	77 933(28)	63 954(46)
C(24)	33 936(51)	79 750(33)	79 652(48)
C(25)	31 132(53)	87 519(35)	87 582(47)
C(26)	23 998(54)	93 597(31)	80 055(49)
C(27)	19 668(48)	91 855(28)	64 240(46)

multiline signal having its maximum *m*/*z* at 1323 for M^+ due to the presence of several isotopes for palladium and chlorine. The computer simulation indicated a similar multiline signal with a maximum at *m*/*z* 1326. From these results it is concluded that the complex **4** is also trinuclear with a Pd_3Cl_6 unit and bidentate ligands similar to those of **5**, although the detailed structure is not known.

Reaction of $Na_2[PdCl_4]$ with 2 equivalents of *o*-$Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N$-2 in aqueous ethanol produced quantitatively yellow needles of the 1 : 2 complex *trans*-$[PdCl_2\{o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N\text{-}2\}_2]$ **7**, where both ligands act as monodentate P donors. The highest-frequency deformation mode of the pyridyl ring [ν(py CN) 1590 cm^{-1}] and the ^1H NMR signal of H^6 of this ring (δ 8.50) were very similar to those observed for the free ligand and support the presence of non-co-ordinated pyridyl groups. The single Pd–Cl stretching frequency at 355 cm^{-1} indicated a *trans* geometry. The corresponding platinum(II) complex *trans*-$[PtCl_2\{o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N\text{-}2\}_2]$ **8** was also obtained selectively in almost quantitative yield from the reaction of $K_2[PtCl_4]$ and 2 equivalents of *o*-$Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N$-2. The *trans* geometry was confirmed by the single Pt–Cl stretching frequency at 342 cm^{-1} and the coupling constant J_{PtP} 2596 Hz.[15] The ^1H NMR spectrum of **7** in CD_2Cl_2 indicated dissociation of the ligand producing the *trans* mononuclear complex **3** [equation (3)]. The equilibrium constant was estimated to be

$$\mathbf{7} \overset{K_{eq}}{\rightleftharpoons} \mathbf{3} + o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N\text{-}2 \quad (3)$$

$K_{eq} = 5.6 \times 10^{-3}$ mol dm^{-3} at 35 °C from the ^1H NMR spectrum. On the contrary the platinum complex **8** did not show dissociation of the ligand in solution and the 1 : 1 complex analogous to **3** could not be obtained even from the reaction of $K_2[PtCl_4]$ and an equimolar amount of the ligand *o*-$Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N$-2 which produces only the 1 : 2 complex **8**. The difference in behaviour between the palladium(II) and platinum(II) complexes may be understood by the difference in the softness of these metals.

Isomerisation of Complex **3**.—On heating the *trans* mononuclear complex **3** in dichloromethane–thf or –diethyl ether at 65 °C for 10 h, it isomerised partially to give the dinuclear complex $[Pd_2Cl_4\{\mu\text{-}o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N\text{-}2\}_2]$ **6** in about 40% yield as estimated from the ^1H NMR spectrum. Recrystallisation of the crude product from dichloromethane–ether gave orange columnar crystals of **6** together with the starting complex **3**. The well formed single crystals of **6** enabled an X-ray structural analysis and the dinuclear structure with the two bridging ligands was clearly established. The ^1H NMR spectrum showed the H^6 proton of the pyridine ring at δ 8.82 with the characteristic complex signal shape indicating the presence of phosphorus in the *trans* position. In the reaction mixture obtained from $[PdCl_2(PhCN)_2]$ with *o*-$Ph_2PC_6H_4CH_2O(CH_2)_3C_5H_4N$-2 in dichloromethane the dinuclear complex **6** was not detected. Heating the *trans* 1 : 1 complex **3** in chloroform under reflux for 5 h also did not produce **6**. Thus, the presence of an O-donor solvent may be necessary for the isomerisation.

X-Ray Crystallographic Studies.—The molecular structure of the *cis*-palladium(II) complex **1** is illustrated in Fig. 1 and selected bond distances and angles are given in Table 5. The *cis* chelate co-ordination of the ligand and almost square-planar co-ordination geometry were confirmed. The Pd–Cl(1) distance is 0.07 Å longer than that of Pd–Cl(2), which clearly reflects the greater *trans* influence of phosphine than that of pyridine. The distance between the ether oxygen and palladium [Pd ··· O 3.036(3) Å] is just the sum of the van der Waals radii[16] of palladium (1.60 Å) and oxygen (1.50 Å) and there may be slight

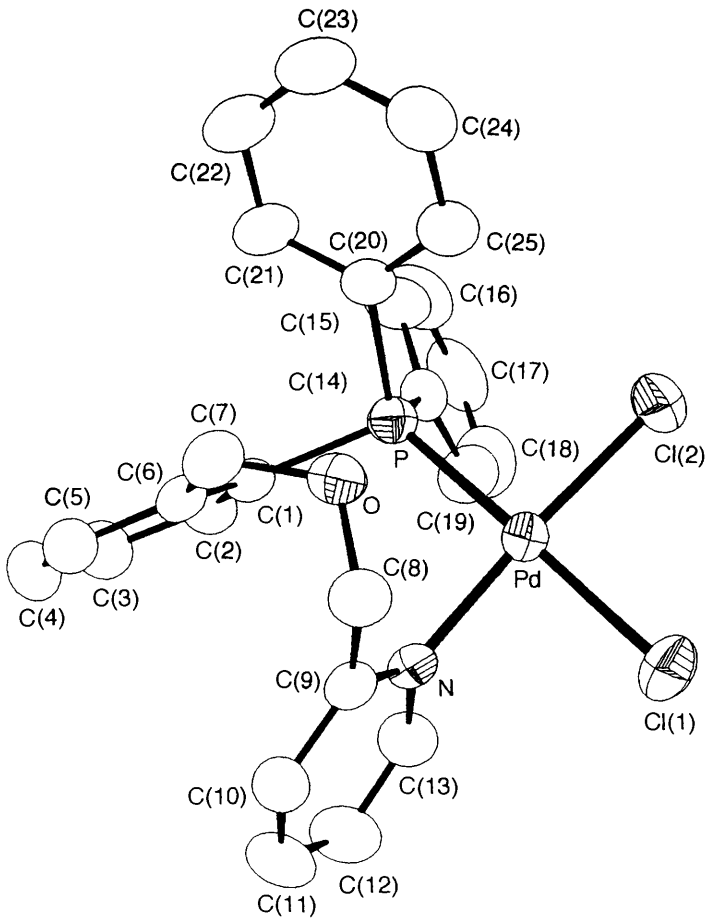


Fig. 1 Perspective view of complex **1**; ORTEP drawing with 50% probability ellipsoids

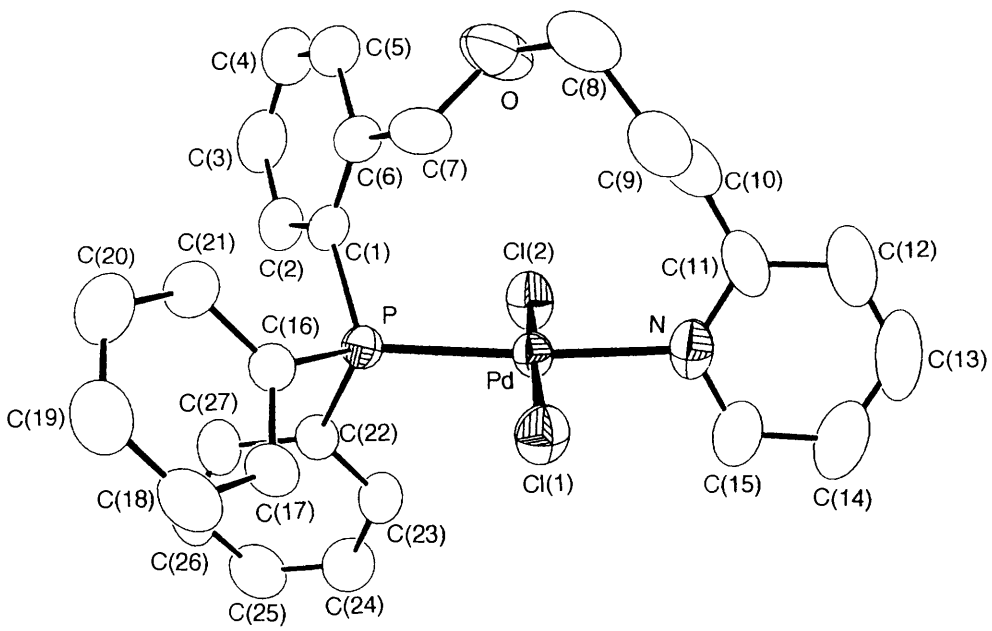


Fig. 2 Perspective view of complex **3** with details as in Fig. 1

interaction between these atoms. Consistently both methylene protons of the ligand backbone appeared as two non-equivalent signals in the ^{1}H NMR spectrum, indicating restricted movement of the backbone due to the presence of the Pd · · · O interaction even in solution. The possibility, however, that even if the Pd · · · O interaction were broken in solution the methylene protons would remain inequivalent due to the barrier to inversion of the nine-membered ring arising from conformational requirements cannot be eliminated completely at present.

The molecular structure of the *trans*-palladium(II) complex **3** is shown in Fig. 2 and selected bond distances and angles are given in Table 6. It reveals a square-planar geometry with the

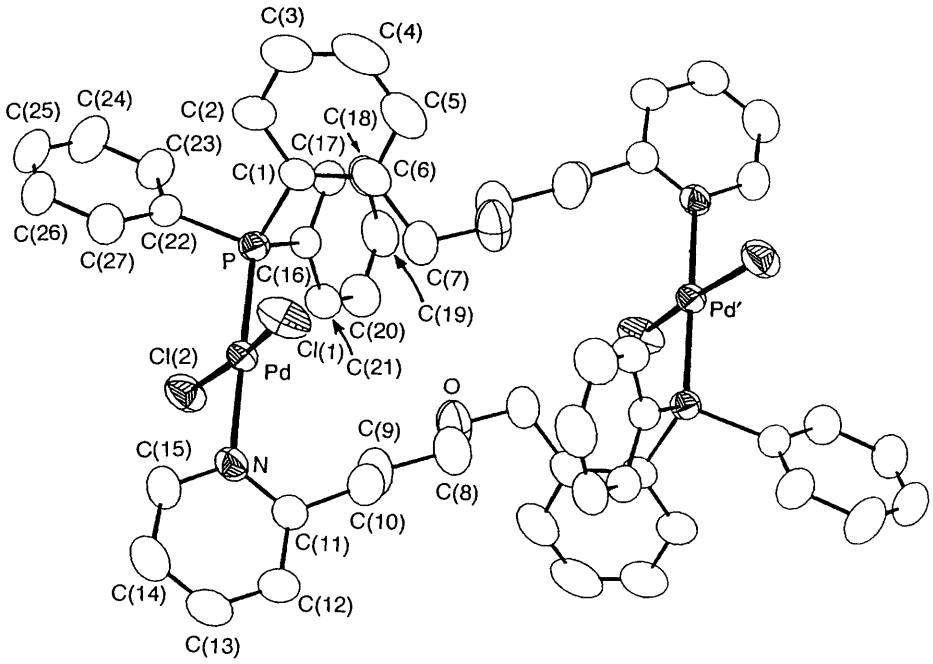


Fig. 3 Perspective view of complex **6** with details as in Fig. 1

Table 4 Fractional atomic coordinates ($\times 10^5$) with e.s.d.s in parentheses for complex **6**

Atom	*x*	*y*	*z*
Pd	46 191(2)	36 163(1)	24 064(1)
Cl(1)	65 252(7)	42 252(6)	21 616(5)
Cl(2)	27 289(8)	29 026(6)	24 518(5)
P	54 471(7)	26 893(4)	34 131(4)
N	38 008(22)	44 909(15)	14 822(13)
O	29 097(27)	52 649(15)	48 274(14)
C(1)	71 146(26)	28 152(19)	37 271(15)
C(2)	79 424(29)	21 617(22)	35 149(19)
C(3)	91 963(33)	22 162(30)	37 815(24)
C(4)	96 263(34)	28 915(34)	42 574(26)
C(5)	88 338(34)	35 596(27)	44 648(21)
C(6)	75 718(28)	35 420(21)	41 830(16)
C(7)	67 924(35)	43 390(22)	43 601(20)
C(8)	34 507(37)	57 390(23)	41 464(21)
C(9)	30 904(37)	53 082(23)	32 754(21)
C(10)	38 779(34)	56 642(20)	25 712(19)
C(11)	35 311(28)	53 180(19)	16 692(17)
C(12)	29 984(32)	58 610(20)	10 213(19)
C(13)	28 085(36)	55 606(23)	1 944(21)
C(14)	30 947(43)	47 252(24)	43(20)
C(15)	35 741(37)	42 082(21)	6 662(18)
C(16)	47 310(25)	26 697(17)	44 757(15)
C(17)	53 746(29)	22 742(19)	51 916(17)
C(18)	48 457(33)	22 574(20)	60 026(17)
C(19)	37 099(35)	26 334(25)	61 137(19)
C(20)	30 960(33)	30 486(26)	54 163(21)
C(21)	35 968(28)	30 630(21)	46 047(18)
C(22)	53 323(27)	15 888(18)	30 022(17)
C(23)	51 518(36)	8 849(21)	35 421(21)
C(24)	51 602(44)	492(23)	32 021(26)
C(25)	53 465(40)	−780(24)	23 384(27)
C(26)	55 033(37)	6 078(25)	17 885(22)
C(27)	54 921(33)	14 484(22)	21 124(20)

Table 5 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for complex **1**

Pd–Cl(1)	2.351(1)	Pd–Cl(2)	2.282(2)
Pd–P	2.254(1)	Pd–N	2.044(4)
P–C(1)	1.837(4)	P–C(14)	1.814(5)
P–C(20)	1.817(5)	O–C(7)	1.425(6)
O–C(8)	1.421(6)	N–C(9)	1.340(6)
C(1)–C(6)	1.409(6)	C(6)–C(7)	1.505(7)
C(8)–C(9)	1.499(7)		
Cl(1)–Pd–Cl(2)	91.63(5)	Cl(1)–Pd–P	177.53(4)
Cl(1)–Pd–N	85.5(1)	Cl(2)–Pd–P	89.54(5)
Cl(2)–Pd–N	176.0(1)	P–Pd–N	93.3(1)
Pd–P–C(1)	113.7(1)	Pd–P–C(14)	108.3(2)
Pd–P–C(20)	120.5(2)	Pd–N–C(9)	122.6(3)
Pd–P–C(1)	113.7(1)	Pd–P–C(14)	108.3(2)
Pd–P–C(20)	120.5(2)	C(1)–P–C(14)	104.5(2)
C(1)–P–C(20)	102.3(2)	C(14)–P–C(20)	106.2(2)
C(1)–C(6)–C(7)	124.6(3)	C(6)–C(7)–O	115.1(4)
C(7)–O–C(8)	112.9(3)	O–C(8)–C(9)	114.5(3)

bidentate ligand spanning *trans* positions. The P–Pd–N and Cl–Pd–Cl are almost linear. The ether oxygen in the ligand does not interact with the central metal atom [Pd · · · O 4.032(4) Å]. In the ^{1}H NMR spectrum each methylene signal of the backbone appears as a singlet, indicating freedom of the movement of the backbone in solution. There was no anomaly in the bond lengths and angles in complex **3**; thus special strain is not present in the chelate ring. As the corresponding *cis*-chelated product could not be obtained, the ligand co-ordinated in *cis* positions must experience much strain and the complex would be labile.

The molecular structure of the binuclear complex **6** is illustrated in Fig. 3 and selected bond distances and angles are listed in Table 7. The two ligands bridge the two palladium atoms and the phosphorus and nitrogen atoms are mutually *trans*. There is no direct interaction between the palladium atoms [Pd · · · Pd′ 9.023 9(5) Å]. The ether oxygens in the ligands do not interact with the palladium atoms. The co-ordination around each palladium atom is again almost square planar and the two co-ordination planes are parallel to each other.

In all these complexes the pyridine ring is almost perpendicular to the molecular plane; dihedral angles between the plane of the pyridine ring and the co-ordination plane are 83.0(1), 102.0(2) and 102.43(9)° for complexes **1**, **3** and **6**, respectively. This geometry seems to result from the configurational demands of the chelating ligands. The Pd–P bond distances are nearly constant regardless of the *trans* ligand

Table 6 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for complex **3**

Pd–Cl(1)	2.293(1)	Pd–Cl(2)	2.307(1)
Pd–P	2.259(1)	Pd–N	2.104(4)
P–C(1)	1.824(4)	P–C(16)	1.831(4)
P–C(22)	1.821(4)	N–C(11)	1.348(7)
N–C(15)	1.32(1)	C(1)–C(6)	1.40(1)
C(6)–C(7)	1.523(7)	C(7)–O	1.393(7)
O–C(8)	1.45(1)	C(8)–C(9)	1.53(1)
C(9)–C(10)	1.535(8)	C(10)–C(11)	1.50(1)
Cl(1)–Pd–Cl(2)	174.85(5)	Cl(1)–Pd–P	94.52(4)
Cl(1)–Pd–N	88.0(1)	Cl(2)–Pd–P	87.35(4)
Cl(2)–Pd–N	90.5(1)	P–Pd–N	175.8(1)
Pd–P–C(1)	109.0(1)	Pd–P–C(16)	120.0(1)
Pd–P–C(22)	112.7(1)	Pd–N–C(11)	122.5(4)
C(1)–P–C(16)	103.7(2)	P–C(1)–C(2)	120.0(2)
P–C(1)–C(6)	120.3(2)	C(1)–P–C(16)	103.7(2)
C(1)–P–C(22)	109.6(2)	C(16)–P–C(22)	101.1(2)
C(1)–C(6)–C(7)	123.1(4)	C(6)–C(7)–O	107.3(4)
C(7)–O–C(8)	113.4(4)	O–C(8)–C(9)	112.3(5)
C(8)–C(9)–C(10)	112.3(5)	C(9)–C(10)–C(11)	113.3(5)
C(10)–C(11)–N	119.3(5)		

Table 7 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for complex **6**

Pd–Cl(1)	2.2925(10)	Pd–Cl(2)	2.3073(9)
Pd–P	2.2549(7)	Pd–N	2.117(2)
P–C(1)	1.836(3)	P–C(16)	1.831(3)
P–C(22)	1.816(3)	N–C(11)	1.344(4)
C(1)–C(6)	1.399(4)	C(6)–C(7)	1.519(5)
O–C(7′)	1.410(5)	O–C(8)	1.420(5)
C(8)–C(9)	1.524(6)	C(9)–C(10)	1.503(5)
C(10)–C(11)	1.511(5)		
Cl(1)–Pd–Cl(2)	171.36(3)	Cl(1)–Pd–P	92.79(3)
Cl(1)–Pd–N	88.38(7)	Cl(2)–Pd–P	89.57(3)
Cl(2)–Pd–N	89.41(7)	P–Pd–N	178.48(7)
Pd–P–C(1)	117.2(1)	Pd–P–C(16)	116.79(9)
Pd–P–C(22)	109.9(1)	Pd–N–C(11)	123.4(2)
Pd–N–C(15)	117.9(2)	P–C(1)–C(2)	118.9(2)
P–C(1)–C(6)	121.9(2)	P–C(16)–C(17)	119.3(1)
P–C(16)–C(21)	121.8(2)	P–C(22)–C(23)	122.5(3)
P–C(22)–C(27)	118.3(2)	C(1)–P–C(16)	102.2(1)
C(1)–P–C(22)	103.8(1)	C(16)–P–C(22)	105.6(1)
C(11)–N–C(15)	118.6(2)	C(1)–C(6)–C(7)	123.9(3)
O–C(8)–C(9)	108.8(3)	C(8)–O–C(7′)	109.9(3)
O–C(7′)–C(6′)	114.0(2)	C(8)–C(9)–C(10)	109.9(4)
C(9)–C(10)–C(11)	113.8(2)	N–C(11)–C(10)	119.0(2)

atoms, 2.254(1)–2.259(1) Å, but Pd–N and Pd–Cl clearly reflect the *trans* influence. Also Pd–N *trans* to P are 0.051–0.064 Å longer than that *trans* to Cl. By changing the *trans* ligand atoms from P to Cl and then to N, the bond distance Pd–Cl becomes successively shorter: 2.282(2) (*trans* to N), 2.317(1) (average, *trans* to Cl), 2.351(1) Å (*trans* to P). From these results the *trans* influence order can be estimated to be P > Cl > N.

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