DALTON

The ditopic ligands 4′-(diphenylphosphino)-2,2′:6′,2″-terpyridine L^1 and 4′-(oxodiphenylphosphanyl)-2,2′:6′,2″-terpyridine L^2: co-ordination to iron(II), ruthenium(II), cobalt(II) and palladium(II); crystal structures of $[RuL^2_2][PF_6]_2\cdot H_2O\cdot MeCN$ and *trans*-$[PdCl_2L^1_2]\cdot 2.5CH_2Cl_2$

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The new compound 4′-(diphenylphosphino)-2,2′:6′,2″-terpyridine L^1 has been prepared; in solution it readily oxidises to the corresponding phosphine oxide, L^2. The reaction between L^1 and $FeCl_2\cdot 4H_2O$ yielded salts containing $[FeL^1_2]^{2+}$, however, oxidation resulted in the formation of $[FeL^2_2]^{2+}$. The corresponding ruthenium(II) complex of L^2 has also been prepared and structurally characterised as the hexafluorophosphate salt; attempts to prepare $[RuL^1_2]^{2+}$ always resulted in oxidation of the ligand to L^2. The reaction of L^1 with cobalt(II) acetate gave $[CoL^1_2]^{2+}$ which has been isolated as the hexafluorophosphate salt. The complexes have been characterised by IR and NMR spectroscopies, mass spectrometry and elemental analysis. Compound L^1 also reacts with $[PdCl_2(NCMe)_2]$ to give *trans*-$[PdCl_2L^1_2]$ which has been fully characterised; results of an X-ray diffraction study confirm the *trans* configuration of the complex.

Metallosupramolecular chemistry involves the use of metal ions in the assembly of multifunctional supramolecules and/or the incorporation of a metal-centred functionality into supramolecules.[1,2] We have developed the 2,2′:6′,2″-terpyridine (terpy) metal-binding domain as a structural motif and building block in metallosupramolecular chemistry,[3,4] and have demonstrated that a wide variety of functional components may be covalently linked to terpy ligands. Co-ordination of such ligands allows variable components to be incorporated into metallosupramolecules. We are currently interested in introducing 'organometallic' functionalities as substituents onto terpy ligands and have recently reported a range of main-group cluster-derivatised ligands.[5–9] We are now extending these studies to the attachment of mono- and poly-nuclear organometallic species to the periphery of terpy ligands. In this paper we describe the preparation of 4′-(diphenylphosphino)-2,2′:6′,2″-terpyridine and the results of our first studies into its co-ordination through the phosphorus or nitrogen donor atoms to mononuclear metal centres.

Experimental

General data

All reactions were carried out under dry argon or dinitrogen and all solvents were distilled before use and were oxygen-free.

The NMR spectra were recorded on Bruker AC 250 or Varian VXR 400 spectrometers; ^{31}P chemical shifts are with respect to δ 0 for 85% H_3PO_4 with downfield shifts positive. The IR measurements were carried out on an ATI Mattson Genesis Series FTIR spectrometer, positive-ion fast atom bombardment mass spectra on a VG ZAB 2SEQ instrument, with 3-nitrobenzyl alcohol as matrix. The matrix assisted laser desorption ionisation (MALDI) time of flight (TOF) mass spectrometric measurements were carried out on a PerSeptive Biosystems Vestec spectrometer in positive linear mode at 15 kV acceleration voltage either without a matrix or with 1,8,9-trihydroxyanthracene as matrix. Electrochemical measurements were performed with an EcoChemie Autolab PGSTAT 20 potentiostat. A conventional three-electrode configuration was used, with glassy carbon working and platinum-bead auxiliary electrodes and a Ag–AgCl reference. For the electrochemical measurements, acetonitrile or dichloromethane, freshly distilled from P_4O_{10}, were used as solvents. The base electrolyte was 0.1 mol dm^{-3} $[NBu^n_4][PF_6]$, recrystallised twice from ethanol–water and thoroughly dried *in vacuo* over P_4O_{10}. Potentials are quoted *vs.* the ferrocene–ferrocenium couple (0.0 V), and referenced to internal ferrocene added at the end of each experiment. Elemental analyses were performed in the Institut für Organische Chemie, Universität Basel. *n*-Butyllithium (1.6 mol dm^{-3} in hexane) was used as supplied by Aldrich and 'ruthenium trichloride trihydrate' from Oxchem; 4′-chloro-2,2′:6′,2″-terpyridine[10] and *trans*-$[PdCl_2(MeCN)_2]$[11] were prepared as described in the literature.

Preparations

4′-(Diphenylphosphino)-2,2′:6′,2″-terpyridine L^1. *n*-Butyllithium (1.37 cm^3; 1.6 mol dm^{-3} in hexane, 2.19 mmol) was added slowly to a solution of PPh_2H (0.40 cm^3, 2.31 mmol) in dry tetrahydrofuran (thf) (10 cm^3). The resultant red solution [characteristic of $Li(PPh_2)$] was cooled to −95 °C. A suspension of 4′-chloro-2,2′:6′,2″-terpyridine (557 mg, 2.08 mmol) in dry thf (100 cm^3) was sonicated and then added dropwise; an intense green colour developed immediately. After complete addition, the solution was allowed to warm and stirred for 12 h at room temperature during which time it became pale yellow and turbid. The solution was then extracted with 1 mol dm^{-3} HCl (2 × 20 cm^3) and the aqueous layer neutralised with 32% aqueous ammonia and extracted with Et_2O (2 × 30 cm^3). The organic layer was dried over $MgSO_4$ and solvent was removed *in vacuo* to give a pale yellow oil which crystallised overnight. Recrystallisation from EtOH yielded L^1 as a white powder (442 g, yield 51%). Solid L^1 (m.p. 143.2–143.9 °C) is stable in air but readily oxidises in solution. NMR ($CDCl_3$): ^1H, δ 8.62–8.56 (m, 4 H, $H^{3,6}$), 8.37 (d, 2 H, J_{PH} 7.3, $H^{3'}$), 7.83 (td, 2 H, *J* 7.5, 2, H^4), 7.50–7.38 (m, 10 H, H^{Ph}) and 7.28 (ddd, 2 H, *J* 7.5, 4, 1, H^5); ^{13}C-{^1H}, δ 121.4 (C^3), 123.7 (C^5), 124.7 (d, J_{PC} 17, $C^{5',3'}$), 128.8 (d, J_{PC} 7, $C^{Ph,3,5}$), 129.3 ($C^{Ph,4}$), 134.3 (d, J_{PC} 20, $C^{Ph,2,6}$), 135.4 (d, J_{PC} 10, $C^{Ph,ipso}$), 136.7 (C^4), 149.2 (C^6), 150.9 (d, J_{PC} 18,

$C^{4'}$), 155.0 (d, J_{PC} 5 Hz, $C^{2'}$) and 156.1 (C^2); ^{31}P-{^{1}H}, δ −4.2. IR (KBr disc): 3057w, 2925w, 2858w, 1577m, 1559s, 1543m, 1478m, 1466m, 1435s, 1385s, 1265w, 1114m, 1097m, 995w, 790m, 744m, 698m, 588s and 508m cm^{-1}. EI mass spectrum: *m*/*z* 417 (100, M^+), 416 (69.4, $M^+ - H$), 339 (19.5, M − Ph) and 262 (6.5%, $M^+ - Ph_2$) (Found: C, 77.4; H, 4.9; N, 10.1. Calc. for $C_{27}H_{20}N_3P$: C, 77.7; H, 4.8; N, 10.1%).

4′-(Oxodiphenylphosphoranyl)-2,2′:6′,2″-terpyridine L^2. Compound L^1 (64.7 mg, 0.155 mmol) and $FeCl_2·4H_2O$ (15.4 mg, 0.12 mmol) were dissolved in EtOH (5 cm^3) and heated at reflux for 2 h to give a deep purple solution. The solvent was then removed *in vacuo* and the solid residue dissolved in water (25 cm^3). Potassium hydroxide (three pellets) was added followed by dropwise addition of 30% H_2O_2 until the purple colour disappeared. The mixture was extracted with CH_2Cl_2 (2 × 15 cm^3) and the combined organic phases were dried over $MgSO_4$. Evaporation of the CH_2Cl_2 solution yielded solid L^2 (56.5 mg, 84% yield; m.p. 215.3–216.2 °C). NMR ($CDCl_3$): ^{1}H, δ 8.80 (d, 2 H, J_{PH} 12.2, $H^{3'}$), 8.65 (dm, 2 H, *J* 5, H^6), 8.60 (dm, 2 H, *J* 8, H^3), 7.85 (td, 2 H, *J* 7.5, 1.5, H^4), 7.84–7.75 (m, 4 H, H^{Ph}), 7.63–7.47 (m, 6 H, H^{Ph}) and 7.33 (ddd, 2 H, *J* 7.5, 5, 1.5, H^5); ^{13}C-{^{1}H} (100 MHz), δ 121.4 (C^3), 123.1 (d, J_{PC} 9, $C^{3'}$), 124.1 (C^5), 128.7 (d, J_{PC} 12, $C^{Ph,3,5}$), 131.2 (d, J_{PC} 104, $C^{Ph,ipso}$), 132.2 (d, J_{PC} 10, $C^{Ph,2,6}$), 132.3 (d, J_{PC} 3, $C^{Ph,4}$), 136.9 (C^4), 143.4 (J_{PC} 97, $C^{4'}$), 149.2 (C^6), 155.2 (C^2) and 155.7 (d, J_{PC} 10 Hz, $C^{2'}$); ^{31}P-{^{1}H}, δ +28.2. IR (KBr): 2924m, 2852w, 1579w, 1560m, 1543m, 1467m, 1435m, 1384m, 1263w, 1191s, 1121s, 1068m, 849w, 821w, 727m, 695s, 594s, 536vs, 502s and 470m cm^{-1}. EI mass spectrum: *m*/*z* 433 (100, M^+), 356 (26, M^+ − Ph) and 77 (5.8%, Ph) (Found: C, 72.0; H, 4.8; N, 9.3. Calc. for $C_{27}H_{20}N_3OP·H_2O$: C, 71.8; H, 4.9; N, 9.3%).

[FeL$^1_2$][PF$_6$]$_2$. Ethanol (5 cm^3) was added to solid L^1 (32.4 mg, 0.078 mmol) and $FeCl_2·4H_2O$ (7.7 mg, 0.039 mmol) under N_2 to give a deep purple solution. The mixture was heated at reflux for 2 h and left stirring at room temperature for 12 h after which $[NH_4][PF_6]$ (50 mg, 0.31 mmol) was added and, after 15 min, the precipitate filtered off and washed with water and MeOH. The product $[FeL^1_2][PF_6]_2$ (42.6 mg, yield 93%) was dried *in vacuo* over P_4O_{10}. NMR (CD_3COCD_3): ^{1}H, δ 8.79 (d, 4 H, J_{PH} 5.4, $H^{3'}$), 8.44 (br d, 4 H, *J* 8, H^3), 7.86 (td, 4 H, *J* 8, 1, H^4), 7.75–7.67 (m, 8 H, H^{Ph}), 7.54–7.50 (m, 12 H, H^{Ph}), 7.37 (br d, 4 H, *J* 5.5, H^6) and 7.12 (ddd, 4 H, *J* 8, 5.5, 1, H^5); ^{31}P-{^{1}H}, δ +4.9 (s) and −138.1 (spt, J_{PF} 708 Hz) (relative integral 1:1). IR (KBr): 3051w, 1604m, 1478m, 1438m, 1435m, 1415m, 1397m, 838vs (PF_6), 787m, 748m, 696m, 592m, 557s (PF_6) and 489w cm^{-1}. TOF mass spectrum: *m*/*z* 890 (FeL^1_2), 472 (FeL^1) and 417 (L^1) (Found: C, 52.8; H, 3.4; N, 7.1. Calc. for $C_{54}H_{40}FeF_{12}N_6P_4·3H_2O$: C, 52.5; H, 3.7; N, 6.8%).

[FeL$^2_2$][PF$_6$]$_2$. Compound L^1 (37.0 mg, 0.089 mmol) and $FeCl_2·4H_2O$ (8.8 mg, 0.0443 mmol) were dissolved in EtOH (3 cm^3) and the solution heated at reflux for 2 h. After further stirring at room temperature for 60 h, 30% H_2O_2 (1 cm^3) was added, followed after 1 h by aqueous $[NH_4][PF_6]$ (80 mg, 0.49 mmol, 3 cm^3 water). The precipitate that formed was filtered through Celite, washed with water and dissolved in MeCN. The solvent was then removed *in vacuo* to give solid $[FeL^2_2][PF_6]_2$ (53.5 mg, >99% yield). NMR (CD_3COCD_3): ^{1}H, δ 9.32 (d, 4 H, J_{PH} 10.8, $H^{3'}$), 8.81 (d, 4 H, *J* 8, H^3), 8.07–7.98 (m, 8 H, H^{Ph}), 7.91 (td, 4 H, *J* 8, 1.5, H^4), 7.71–7.58 (m, 12 H, H^{Ph}), 7.39 (br d, 4 H, *J* 5, H^6) and 7.10 (ddd, 4 H, *J* 8, 5, 1.5, H^5); ^{31}P-{^{1}H}, δ +30.1 (s) and −138.1 (spt, J_{PF} 708 Hz) (relative integral 1:1). IR (KBr): 3060w, 2924w, 1606m, 1438m, 1416m, 1190m, 1121m, 1027w, 840vs (PF_6), 790m, 752m, 728m, 702m, 597m, 583w, 558s (PF_6) and 499w cm^{-1}. TOF mass spectrum: *m*/*z* 920 (FeL^2_2), 490 (FeL^2) and 433 (L^2) (Found: C, 51.3; H, 3.8; N, 6.7; O, 6.4. Calc. for $C_{54}H_{40}FeF_{12}N_6O_2P_4·3H_2O$: C, 51.2; H, 3.6; N, 6.6; O, 6.3%).

[RuL$^2_2$][PF$_6$]$_2$. Commercial $RuCl_3·3H_2O$ (16.9 mg, 0.065 mmol) and compound L^2 (56.1 mg, 0.129 mmol) were placed in a flask and covered with ethane-1,2-diol (3 cm^3) and EtOH (0.5 cm^3). The mixture was heated to 80 °C for 12 h and then a solution of $[NH_4][PF_6]$ (136 mg, 1 mmol) in water (5 cm^3) was added. The resulting precipitate was separated on Celite, and washed with water and EtOH, and then dissolved in MeCN. Evaporation of the solvent yielded $[RuL^2_2][PF_6]_2$ (70 mg, 86% yield). NMR (CD_3COCD_3): ^{1}H, δ 9.15 (d, 4 H, J_{PH} 11.2, $H^{3'}$), 8.80 (br d, 4 H, *J* 8, H^3), 8.03–7.89 (m, 12 H, H^{Ph}, H^4), 7.72–7.56 (m, 16 H, H^6, H^{Ph}) and 7.19 (ddd, 4 H, *J* 8, 5.5, 1.5, H^5); ^{31}P-{^{1}H}, δ +30.4 (s) and −138.1 (spt, J_{PF} 708 Hz) (relative integral 1:1). IR (KBr): 3060w, 2924w, 1604w, 1439m, 1414m, 1340w, 1288w, 1187m, 1121m, 1028w, 840vs (PF_6), 788m, 751m, 701m, 596m and 557s cm^{-1} (PF_6). TOF mass spectrum: *m*/*z* 1115 ($RuL^2_2PF_6$), 967 (RuL^2_2), 890 (RuL^2_2 − Ph), 843 [RuL^2_2 − P(O)Ph], 766 [RuL^2(terpy)] and 534 (RuL^2) (Found: C, 50.5; H, 3.4; N, 7.3; O, 4.1. Calc. for $C_{54}H_{40}F_{12}N_6O_2P_4Ru·1.5H_2O·$MeCN: C, 50.7; H, 3.5; N, 7.4; O, 4.2%).

[CoL$^1_2$][PF$_6$]$_2$. Degassed EtOH (5 cm^3) was added to solid L^1 (37.2 mg, 0.089 mmol) and $Co(O_2CMe)_2·4H_2O$ (11.1 mg, 0.045 mmol) to give an orange solution. The mixture was heated at reflux for 12 h under dinitrogen after which $[NH_4][PF_6]$ (80 mg, 0.49 mmol) was added; after 15 min the precipitate was filtered through Celite and washed with water and EtOH. The precipitate was redissolved in MeCN and the solvent removed *in vacuo*. The product was dried *in vacuo* over P_4O_{10} yielding $[CoL^1_2][PF_6]_2$ (48.0 mg, 91%). NMR (CD_3COCD_3): ^{1}H, δ 95.4 (4 H), 55.3 (4 H), 43.1 (4 H), 33.3 (4 H), 10.6 (8 H), 9.2 (4 H), 8.6 (8 H) and 8.3 (4 H); ^{31}P-{^{1}H}, δ −4.0 (s) and −138.1 (spt, J_{PF} 708 Hz) (relative integral 1:1). IR (KBr): 1600m, 1570vw, 1542vw, 1472w, 1436vw, 1411w, 1243vw, 1162vw, 838vs (PF_6^-), 788m, 747w, 699w, 591w and 557s cm^{-1} (PF_6^-). TOF mass spectrum: *m*/*z* 925 (CoL^2_2 +2O), 909 (CoL^1_2 + O), 893 (CoL^1_2), 494 (CoL^1 + F) and 475 (CoL^1) (Found: C, 53.8; H, 3.5; N, 7.1. Calc. for $C_{54}H_{40}CoF_{12}N_6P_4·H_2O$: C, 54.0; H, 3.5; N, 7.0%).

[PdCl$_2$L$^1_2$]. Compound L^1 (31.8 mg, 0.076 mmol) was added to a suspension of *trans*-$[PdCl_2(MeCN)_2]$ (9.9 mg, 0.038 mmol) in CH_2Cl_2 (2.5 cm^3) and stirred at room temperature for 24 h. The bright yellow product was precipitated by addition of pentane (2.5 cm^3) and dried *in vacuo* over P_4O_{10} to give $[PdCl_2L^1_2]$ as a yellow solid (23.0 mg, 61% yield). NMR ($CDCl_3$): ^{1}H, δ 8.75 (t, 4 H, *J* 6, $H^{3'}$), 8.63 (dm, 4 H, *J* 4, H^6), 8.55 (d, 4 H, *J* 8, H^3), 7.95–7.86 (m, 8 H, H^{Ph}), 7.81 (td, 4 H, *J* 8, 1.5, H^4), 7.50–7.39 (m, 12 H, H^{Ph}) and 7.29 (ddd, 4 H, *J* 7.5, 5, 1.5 Hz, H^5); ^{31}P-{^{1}H}, δ +21.2. IR (KBr): 3056w, 3013w, 1576s, 1558vs, 1537m, 1466m, 1434m, 1383s, 1263w, 1123w, 1110w, 1091w, 1071w, 995w, 789s, 747s, 698s, 678w, 659w, 590m and 504w cm^{-1}. FAB mass spectrum: *m*/*z* 975 ($PdClL^1_2$), 940 (PdL^1_2), 598 ($PdCl_2L^1$), 558 ($PdClL^1$) and 523 (PdL^1) (Found: C, 62.6; H, 3.9; N, 8.1. Calc. for $C_{54}H_{40}Cl_2N_6P_2Pd·0.33CH_2Cl_2$: C, 62.7; H, 3.9; N, 8.1%).

Crystallography

Yellow needles of *trans*-$[PdCl_2L^1_2]·2.5CH_2Cl_2$ were grown by diffusion of pentane into a dichloromethane solution; the crystals lose solvent very readily to give a yellow powder. Dark red cubes of $[RuL^2_2][PF_6]_2·H_2O·$MeCN were grown by diffusion of Et_2O into an acetonitrile solution.

Crystal data. $C_{54}H_{40}Cl_2N_6P_2Pd·2.5CH_2Cl_2$, yellow needle, crystal size 0.20 × 0.25 × 0.70 mm, M = 1224.54, triclinic, space group $P\bar{1}$, a = 12.683(2), b = 15.407(2), c = 16.965(4) Å, α = 114.03(1), β = 94.63(1), γ = 112.49(1)°, U = 2685.5(9) Å^3, $F(000)$ = 1242, Z = 2, D_c = 1.51 g cm^{-3}.

$C_{54}H_{40}RuN_6O_2P_2·2PF_6·CH_3CN·H_2O$, dark red cube, crystal size 0.42 × 0.45 × 0.55 mm, M = 1316.96, monoclinic, space

group $P2_1/a$, $a = 16.830(2)$, $b = 20.593(2)$, $c = 17.630(1)$ Å, $\beta = 110.868(8)°$, $U = 5709(1)$ Å^3, $F(000) = 2664$, $Z = 4$, $D_c = 1.53$ g cm^{-3}.

Data collection and refinement. The crystal selected for structure determination was stuck with oil on to a glass fibre; the determination for $[RuL^2_2][PF_6]_2 \cdot H_2O \cdot MeCN$ was carried out at 293 K, and the crystal of $[PdCl_2L^1_2] \cdot 2.5CH_2Cl_2$ was cooled to 193 K using an Oxford Cryostream low-temperature device. Unit-cell parameters were determined by the least-squares method using 25 (for the ruthenium complex) and 21 (for the palladium complex) carefully centred independent reflections. Data collection was carried out on a four-circle Enraf-Nonius CAD4 diffractometer using monochromated Cu-Kα radiation ($\lambda = 1.541\,80$ Å). The ω–2θ technique was used to measure, for $[RuL^2_2][PF_6]_2 \cdot H_2O \cdot MeCN$, 8033 reflections in the range $4 \leqslant 2\theta \leqslant 133.5°$ and for $[PdCl_2L^1_2] \cdot 2.5CH_2Cl_2$ 7115 reflections, range $4 \leqslant 2\theta \leqslant 118°$. Three standard reflections monitored every hour during data collection showed a decay of 1.77% for $[PdCl_2L^1_2] \cdot 2.5CH_2Cl_2$ which was corrected for during data reduction, and 78.65%, but fairly linear, decay for $[RuL^2_2][PF_6]_2 \cdot H_2O \cdot MeCN$. For $[RuL^2_2][PF_6]_2 \cdot H_2O \cdot MeCN$, the 6720 unique data with $I \geqslant 3\sigma(I)$ were used to solve and refine the structure; for $[PdCl_2L^1_2] \cdot 2.5CH_2Cl_2$, the 5992 unique data with $I \geqslant 2\sigma(I)$, were used. The usual corrections were applied. The absorption correction was determined by DIFABS[12] in both cases: $[RuL^2_2][PF_6]_2 \cdot H_2O \cdot MeCN$ and $[PdCl_2L^1_2] \cdot 2.5CH_2Cl_2$, the maximum and minimum transmissions were 1.00, 0.42 and 1.00, 0.32 respectively.

Structural analysis and refinement. The structures were solved by direct methods using the program SIR 92.[13] Anisotropic least-squares refinement was carried out on all non-hydrogen atoms except those of the solvent molecules using the program CRYSTALS.[14] The hydrogen atoms were placed in calculated positions with a fixed distance of 1.0 Å. Scattering factors were taken from ref. 15.

$[RuL^2_2][PF_6]_2 \cdot H_2O \cdot MeCN$. The structure contains, apart from the $[PF_6]^-$ anions, one MeCN and one H_2O. Two halves of one $[PF_6]^-$ anion are situated on two different centres of symmetry; they are well behaved. The other $[PF_6]^-$ anion, together with the MeCN molecule, is disordered. Refinement was carried out using appropriate restraints. Final values of R' (0.0624) and R (0.0538) were obtained. The residual peaks (maximum 0.94 e Å^{-3}) in the difference map are within what is acceptable for a structure containing a metal centre, and more or less all of them are located near the Ru. Selected bond lengths and angles are presented in Table 1.

$[PdCl_2L^1_2] \cdot 2.5CH_2Cl_2$. Dichloromethane molecules are located in the cavities between the complex molecules. Two of the solvent molecules are disordered; one is located near a centre of symmetry. They were refined using split models. The final R values were 0.0920 (R) and 0.0970 (R'), and the final Fourier-difference maps contained relatively large peaks (2.63 e Å^{-3}) only in the region of the disordered solvent molecules and around the palladium centre. Selected bond lengths and angles are presented in Table 2.

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.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/543.

Results and Discussion

Ligand synthesis

Our interests in combining terpy metal-binding domains with cluster components has led us to devise new ditopic ligands which contain both hard and soft donor sets. The spatial separation and organisation of the hard and soft domains removes the ambiguities found earlier[16–22] and allows a clear and concise coding of the donor sets. We planned to use phosphine substituents as the soft donor set for the subsequent binding of mono- and poly-nuclear low-oxidation-state metal carbonyl complexes. Although a variety of phosphine-functionalised oligopyridines are known,[16,18,21,22] we decided to prepare the new ligand L^1 in which the tridentate hard N_3-donor set is in a linear arrangement with respect to the soft phosphorus donor.

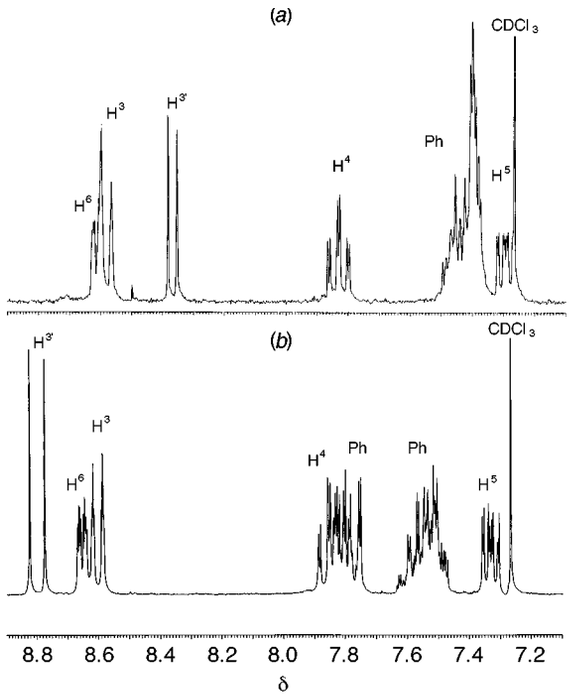
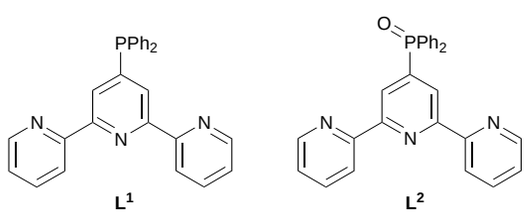


Fig. 1 The 250 MHz ^{1}H NMR spectra (300 K, $CDCl_3$) of (*a*) L^1 and (*b*) L^2



We considered two strategies for the synthesis of ligand L^1. In the first, we planned the introduction of the PPh_2 moiety by the reaction of electrophilic PPh_2Cl with a 2,2′:6′,2″-terpyridin-4′-yl anion whereas in the second approach a nucleophilic $[PPh_2]^-$ anion would be treated with an electrophilic 4′-halogeno-2,2′:6′,2″-terpyridine. After numerous unsuccessful attempts at forming 4′-lithio-2,2′:6′,2″-terpyridine by direct lithiation of 2,2′:6′,2″-terpyridine with a variety of alkyl- and aryl-lithium reagents or by lithiation or translithiation of 4′-chloro-2,2′:6′,2″-terpyridine, we centred our efforts upon the second approach.

Solutions of $Li(PPh_2)$ were prepared *in situ* by the reaction of PPh_2H with *n*-butyllithium and were subsequently treated with 4′-chloro-2,2′:6′,2″-terpyridine. The red colour of the phosphane anion was discharged upon the addition of the 4′-chloro-2,2′:6′,2″-terpyridine and after work-up L^1 was obtained as a white microcrystalline solid in 51% yield. Compound L^1 was fully characterised by spectroscopic and analytic methods. The most pertinent data were the observation of a parent ion at *m*/*z* 417 in the EI mass spectrum and the expected ^{1}H and ^{13}C NMR spectra. The ^{13}C NMR spectrum exhibited typical couplings $^1J(P–C^{4'})$ 18 Hz between the phosphorus and the carbon atoms of the directly bonded pyridine ring. The ^{1}H NMR spectrum of a $CDCl_3$ solution of L^1 is presented in Fig. 1(*a*). The most

characteristic feature is the observation of $H^{3'}$ as a doublet with $^3J_{PH}$ of 7.3 Hz. Free L^1 is characterised in its ^{31}P-{^1H} NMR spectrum by a signal at δ −4.2, typical of a triarylphosphine (*e.g.* PPh_3, δ −6.0). Both the ^1H and ^{13}C NMR spectra confirm the expected symmetry of the molecule in solution.

Solid compound L^1 is stable in air, but in solution it readily oxidises to the corresponding phosphine oxide L^2. Compound L^2 may be prepared directly from the oxidation of co-ordinated L^1 in $[FeL^1_2]^{2+}$ with hydrogen peroxide. Subsequent demetallation[23] yielded the free oxide L^2 in good yield. Once again the ^1H and ^{13}C NMR spectra were in full accord with the proposed structure. The most obvious feature in the ^{13}C NMR signal on going from L^1 to L^2 is the expected increase of the $^1J_{PC}$ coupling constants from 10–20 Hz for L^1 to ≈100 Hz for L^2.[24] The ^{31}P-{^1H} NMR spectrum of L^2 exhibits a single resonance at δ +28.2; the downfield shifting upon conversion of a phosphine into a phosphine oxide is characteristic (for example, $OPPh_3$ is found at δ +24). The ^1H NMR spectrum of a $CDCl_3$ solution of L^2 is presented in Fig. 1(*b*). Once again, the appearance of $H^{3'}$ as a doublet is a characteristic feature. A number of trends are apparent. As expected, the $^3J_{PH}$ coupling to $H^{3'}$ increases from 7.3 for L^1 to 12.2 Hz for L^2. There is also a significant downfield shifting of $H^{3'}$, H^3 and the *ortho*-protons of the phenyl rings on passing from the phosphorus(III) compound L^1 to the phosphorus(V) derivative L^2. The remaining resonances are only slightly affected by the oxidation of the phosphorus.

Complex formation between L^1 and L^2 and iron(II) and ruthenium(II)

The reactions of compound L^1 with certain metal centres is likely to be accompanied by competition for the binding of the *P*- or *N*,*N*′,*N*″-donor sets and choice of metal centre based upon hard or soft behaviour is crucial to the controlled assembly of complexes containing L^1. Of course, the oxidised ligand L^2 has lost the potential for co-ordination through the phosphorus donor, but may function as either an *O*- or *N*,*N*′,*N*″-donor.

The reaction of L^1 with hydrated iron(II) chloride leads to the formation of deep purple solutions containing the cation $[FeL^1_2]^{2+}$ which may be isolated as the diamagnetic hexafluorophosphate salt, $[FeL^1_2][PF_6]_2$. The ^{31}P NMR spectrum of the isolated complex clearly indicates that only the nitrogen donor atoms are co-ordinated, since co-ordination is accompanied by only a very small shift in the ^{31}P NMR spectroscopic signal from δ −4.2 for free L^1 to +4.9; a septet assigned to the $[PF_6]^-$ ion was also observed. The relative integrals of the signals was 1:1. This indicates that the PPh_2 groups are equivalent and are in a pendant rather than co-ordinated mode, and is fully consistent with the expectation that the iron(II) centre will preferentially bind two equivalents of L^1 to give six-co-ordination of nitrogen donors. Additional evidence for this co-ordination mode comes from the electronic spectrum which exhibits a metal-to-ligand charge-transfer (MLCT) absorption at 567 nm (ε 21 700 $dm^3\ mol^{-1}\ cm^{-1}$); this value is considerably higher than that of $[Fe(terpy)_2]^{2+}$ but is consistent with known substituent effects in $[M(terpy)_2]^{2+}$ complexes.[25] The ^1H NMR spectrum of a CD_3COCD_3 solution of $[FeL^1_2][PF_6]_2$ is presented in Fig. 2(*a*). The co-ordination of the terpy domain to the metal is further established by the similarity of the spectrum to that of $[Fe(terpy)_2]^{2+}$ salts. The characteristic features are the observation of $H^{3'}$ and H^3 shifted to lowest field as a result of van der Waals deshielding and the upfield shifting of H^6, which lies above the shielding region of the other terpy ligand, with respect to free L^1. The proposed structure of the $[FeL^1_2]^{2+}$ cation is shown in Fig. 3. This complex is, in effect, a metallogue of a linear dinucleating phosphine such as 1,2-bis(diphenylphosphino)ethyne, in which the terminal phosphino-groups have the potential for co-ordination to low-oxidation-state

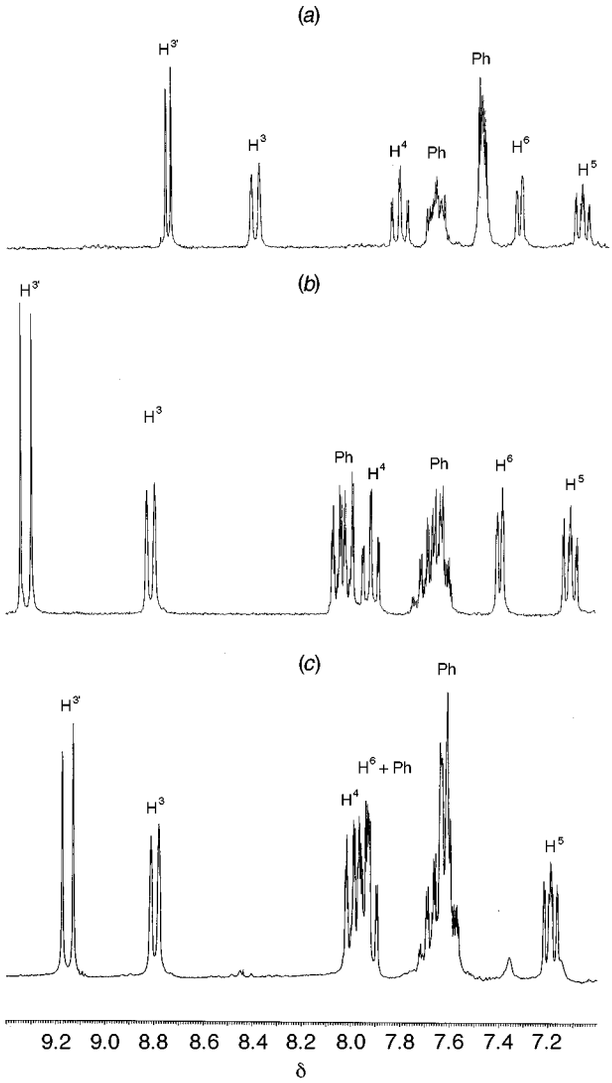


Fig. 2 The 250 MHz ^1H NMR spectra (300 K, CD_3COCD_3) of (*a*) $[FeL^1_2][PF_6]_2$, (*b*) $[FeL^2_2][PF_6]_2$ and (*c*) $[RuL^2_2][PF_6]_2$

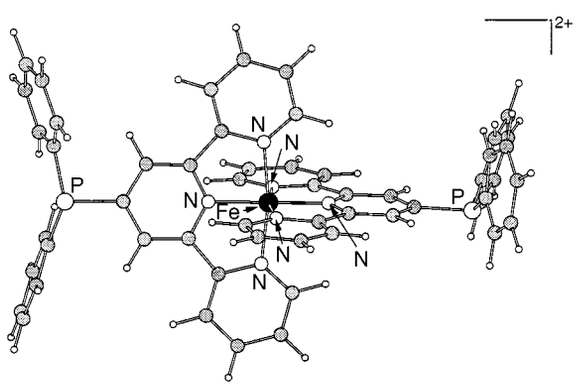


Fig. 3 Proposed structure of the $[FeL^1_2]^{2+}$ cation

metal centres and transition-metal clusters and we are currently investigating such reactions.

The reaction between L^1 and $FeCl_2{\cdot}4H_2O$ under N_2 followed by treatment with hydrogen peroxide results in the oxidation of the PPh_2 groups and the complex $[FeL^2_2][PF_6]_2$ is isolated in near-quantitative yield. The ^{31}P-{^1H} NMR spectrum showed a singlet at δ +30.1 (close to that of free L^2) in addition to a septet for the $[PF_6]^-$ ion. The co-ordination shifts [Δδ = δ (ligand, $CDCl_3$) − δ (complex, CD_3COCD_3)] of −9.1 (L^1) and −1.9 (L^2) are reasonably similar and indicate similar co-ordination modes. The electronic spectrum again exhibits an

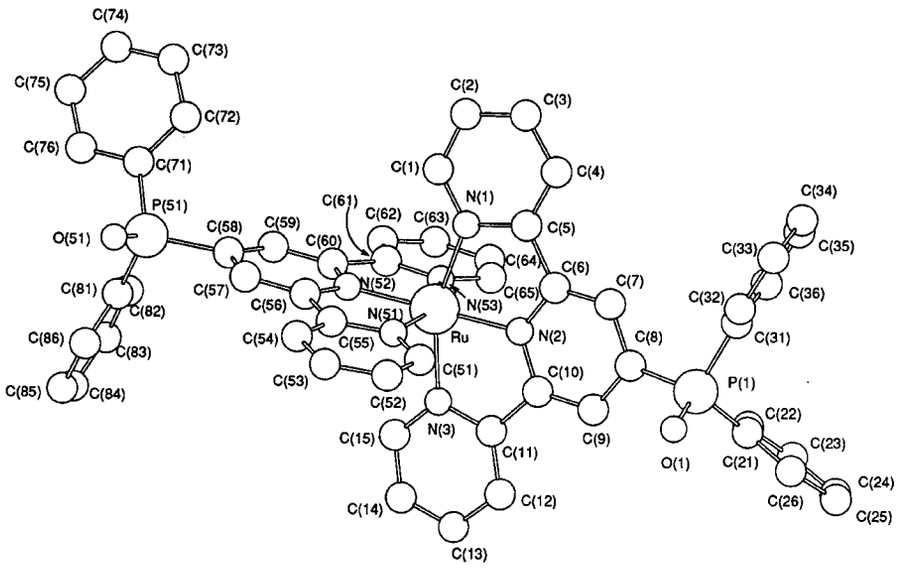


Fig. 4 Structure of the cation $[RuL^2_2]^{2+}$ determined for the compound $[RuL^2_2][PF_6]_2\cdot H_2O\cdot MeCN$. Hydrogen atoms are omitted for clarity

MLCT band 568 nm (ε 22 000 $dm^3\ mol^{-1}\ cm^{-1}$), again consistent with the N_6 environment about the iron. Fig. 2(*b*) shows the ^1H NMR spectrum of $[FeL^2_2][PF_6]_2$. The most significant features are the downfield shifting of $H^{3'}$ and H^3, the protons which are closest to the phosphorus centre. The *ortho*-protons of the phenyl groups are similarly downfield shifted but the remaining protons of the terminal terpy rings are effectively constant in the complexes of L^1 and L^2. As expected, the $^3J_{PH}$ coupling constant increases significantly on oxidation of the phosphorus.

The two iron complexes are electrochemically active and have been studied by cyclic voltammetry. Acetonitrile solutions of $[FeL^1_2][PF_6]_2$ exhibit a reversible iron(II)–iron(III) process at +0.79 V and two near-reversible ligand-centred reductions at −1.54, −1.69 V (all potentials *versus* ferrocene–ferrocenium), whereas the complex $[FeL^2_2][PF_6]_2$ shows a reversible iron(II)–iron(III) process at +0.85 V and two quasi-reversible ligand reductions at −1.39, −1.54 V. The ligand L^1 in $[FeL^1_2][PF_6]_2$ is slightly electron withdrawing to about the same extent as a chloro substituent in the same position with a calculated σ^+ value of +0.14[23,26] {$[Fe(terpy)_2][PF_6]_2$, +0.74 V; $[Fe(Clterpy)_2][PF_6]_2$, (Clterpy = 4-chloro-2,2′:6′,2″-terpyridine) +0.78 V}, presumably as a result of the tetrahedral geometry at the phosphorus preventing significant phosphorus-ligand π* overlap. In contrast, the phosphine oxide is strongly electron withdrawing and significantly destabilises the iron(III) state; the calculated σ^+ value is +0.41.

Attempts to form the complexes $[RuL^1_2]^{2+}$ or $[RuL^1(terpy)]^{2+}$ under a range of experimental conditions were unsuccessful. The use of ruthenium(III) chloro complexes as starting materials invariably led to partial or complete oxidation to give complexes of L^2. In addition, mixtures of complexes with N_3- and *P*-bonded ligands were obtained. However, the reaction of ruthenium(III) chloride trihydrate with 2 equivalents of L^2 in ethane-1,2-diol–EtOH leads to the formation of the cation $[RuL^2_2]^{2+}$ which has been isolated as the orange-red hexafluorophosphate salt $[RuL^2_2][PF_6]_2$ in 86% yield. The ^{31}P NMR spectrum of this complex exhibits two signals assigned to the anion (δ −138.1, spt) and to equivalent O=PPh_2 groups (singlet, δ +30.4). The similarity of the latter shift with that of the complex $[FeL^2_2][PF_6]_2$ indicates similar structures with the phosphine oxide groups pendant. The ^1H NMR spectrum of $[RuL^2_2][PF_6]_2$ [Fig. 2(*c*)] closely resembles that of $[FeL^2_2][PF_6]_2$ with the exception that H^6, which lies closest to the metal, is shifted downfield slightly. The chemical shifts of the protons on the terminal pyridine rings closely resemble those observed for $[Ru(terpy)_2][PF_6]_2$.

Table 1 Selected bond distances (Å) and angles (°) for $[RuL^2_2][PF_6]_2\cdot H_2O\cdot MeCN$

Ru–N(1)	2.065(4)	Ru–N(2)	1.988(3)
Ru–N(3)	2.065(4)	Ru–N(51)	2.068(4)
Ru–N(52)	1.992(3)	Ru–N(53)	2.071(4)
N(1)–C(1)	1.336(6)	N(1)–C(5)	1.378(6)
N(2)–C(6)	1.345(5)	N(2)–C(10)	1.356(5)
N(3)–C(15)	1.331(6)	N(3)–C(11)	1.367(6)
P(1)–O(1)	1.487(4)	P(1)–C(21)	1.785(5)
P(1)–C(31)	1.789(5)	P(1)–C(8)	1.810(5)
N(51)–C(51)	1.349(6)	N(53)–C(65)	1.346(6)
N(51)–C(55)	1.362(6)	N(52)–C(56)	1.360(6)
N(52)–C(60)	1.350(6)	N(53)–C(61)	1.362(6)
P(51)–C(58)	1.831(4)	P(51)–O(51)	1.481(4)
P(51)–C(71)	1.798(5)	P(51)–C(81)	1.796(5)
N(1)–Ru–N(2)	79.0(1)	N(1)–Ru–N(3)	157.9(2)
N(2)–Ru–N(3)	79.0(1)	N(1)–Ru–N(51)	93.6(1)
N(2)–Ru–N(51)	96.4(1)	N(3)–Ru–N(51)	90.8(1)
N(1)–Ru–N(52)	99.8(1)	N(2)–Ru–N(52)	175.6(1)
N(3)–Ru–N(52)	102.3(1)	N(51)–Ru–N(52)	79.5(1)
N(1)–Ru–N(53)	91.9(1)	N(2)–Ru–N(53)	105.9(1)
N(3)–Ru–N(53)	92.2(1)	N(51)–Ru–N(53)	157.7(1)
N(52)–Ru–N(53)	78.3(1)	C(58)–P(51)–O(51)	109.7(2)
C(58)–P(51)–C(71)	108.8(2)	O(51)–P(51)–C(71)	113.2(2)
C(58)–P(51)–C(81)	105.9(2)	O(51)–P(51)–C(81)	112.5(2)
C(71)–P(51)–C(81)	106.4(2)	C(8)–P(1)–O(1)	110.1(2)
C(8)–P(1)–C(21)	107.6(2)	O(1)–P(1)–C(21)	114.1(2)
C(8)–P(1)–C(31)	106.6(2)	O(1)–P(1)–C(31)	112.2(2)
C(21)–P(1)–C(31)	105.8(2)		

The cyclic voltammogram of an acetonitrile solution of $[RuL^2_2][PF_6]_2$ exhibits a single, fully reversible ruthenium(II)–ruthenium(III) process at +1.03 V and two reversible ligand-centred reductions at −1.42 and −1.65 V. Once again, this indicates that L^2 is a significantly electron-withdrawing ligand, equivalent to our recently described paraquat metallogue.[27–29]

Crystal structure of $[RuL^2_2][PF_6]_2\cdot H_2O\cdot MeCN$

Dark red cubes of $[RuL^2_2][PF_6]_2\cdot H_2O\cdot MeCN$ were obtained by the slow evaporation of an acetonitrile solution. The structure of the cation $[RuL^2_2]^{2+}$ is shown in Fig. 4 and selected bond distances and angles are listed in Table 1. The crystallographic data confirm the co-ordination mode of each ligand L^2 as being through the three nitrogen donor atoms, and the meridional co-ordination environment is as expected. All distances and angles within the ligand and co-ordination sphere of the ruthenium(II) centre are unexceptional.[23] The structure also confirms the

presence of phosphine oxide rather than phosphine substituents. Fig. 4 shows that both P=O units are orientated on the same side of the ruthenium(II) centre and this orientation may be enforced by the fact that atom O(51) is involved in a hydrogen-bonding interaction to the solvate water molecule [O(51)···O_{water} 2.765 Å]. The P=O distance in the phosphine oxide which is not hydrogen bonded to water of 1.487(4) Å is typical of triphenylphosphine oxide (1.462–1.495 Å)[30] and of the orthorhombic form of triphenylphosphine oxide hemihydrate which contains no hydrogen-bonding interactions with water (P–O 1.485 Å).[31] The hydrogen-bonded P=O bond length of 1.481(4) Å is very similar to that in the monoclinic form of triphenylphosphine oxide hemihydrate (1.483 Å)[32] and the O_P···O_{water} distance of 2.765 Å is actually shorter than that in the hemihydrate (2.910 Å). The terpyridine-P skeleton is essentially planar in the hydrogen-bonded ligand but is slightly bowed in the other; this is attributed to crystal-packing effects.

Complex formation between L^1 and cobalt(II)

The reaction between L^1 and hydrated cobalt(II) acetate followed by anion exchange with ammonium hexafluorophosphate led to the formation of $[CoL^1_2][PF_6]_2$ in high yield. The ^{1}H NMR spectrum of the complex exhibited paramagnetically shifted resonances for those protons of the terpy moiety typical of a low-spin solution species.[33] This provides evidence for co-ordination through the *N*,*N*′,*N*″-donor set rather than the phosphino units and is supported by the observation in the ^{31}P NMR spectrum of a singlet at δ −4.0 (close to that of free L^1) in addition to the signals assigned to the $[PF_6]^-$ anion. The compound $[CoL^1_2][PF_6]_2$ is relatively stable in the solid state but readily oxidises in solution. The ^{1}H NMR spectrum of a sample which has been standing in solution shows the growth of signals close to those assigned to $[CoL^1_2]^{2+}$, and the retention of the paramagnetic shifts indicates that the oxidation is ligand-centred to give L^2 rather than cobalt-centred to give a diamagnetic, low-spin cobalt(III) species. The cyclic voltammogram of an acetonitrile solution of $[CoL^1_2][PF_6]_2$ shows, as expected, a near-reversible cobalt(II)–cobalt(III) process at −0.091 V.

Complex formation between L^1 and palladium(II)

Metal centres such as palladium(II) or platinum(II) are expected preferentially to co-ordinate to the soft phosphorus-donor atom of ligand L^1. The reaction of L^1 with *trans*-$[PdCl_2(MeCN)_2]$ leads to the formation of the yellow complex $[PdCl_2L^1_2]$. In its TOF mass spectrum the highest-mass peaks corresponded to the fragment $PdClL^1_2$ and no parent ion was observed. A single resonance is observed in the ^{31}P NMR spectrum and the downfield shift from δ −4.2 for the free L^1 to δ +21.2 is consistent with co-ordination to palladium through the phosphorus-donor atoms, and that both ligands are equivalent. Furthermore, the observation of single ^{31}P environment argues strongly for the formation of a single *cis* or *trans* isomer.

The ^{1}H NMR spectrum of $[PdCl_2L^1_2]$ in $CDCl_3$ confirms the high symmetry of the product and also indicates the presence of only one *cis* or *trans* isomer. The most conspicuous and initially unexpected feature is the observation of an apparent triplet at δ 8.75 (*J* 6 Hz) corresponding to the $H^{3'}$ protons. Initial suspicions that this might be due to the $H^{3'}$ protons existing as various conformers were eliminated by recording the spectrum at both 250 and 400 MHz fields. In each case a coupling constant of 6 Hz was obtained. It is one of the features of ^{31}P NMR spectra that short- and long-range coupling constants may possess similar magnitudes and in this case a careful analysis of the spin system provides an explanation. A given $H^{3'}$ proton is expected to couple to two magnetically different (but chemically identical) phosphorus nuclei; the proton spectrum will exhibit $^3J_{PH}$ (to the phosphorus in the same ligand) and $^5J_{PH}$ (to the phosphorus of the other ligand) couplings. In this case the magnitude of the two coupling constants is very similar leading to the apparent triplet. This is characteristic of a *trans* configuration for the square-planar complex in solution.[34] In order to confirm this stereochemistry, we have determined the solid-state structure of $[PdCl_2L^1_2]$.

Table 2 Selected bond distances (Å) and angles (°) for *trans*-$[PdCl_2L^1_2]\cdot 2CH_2Cl_2$

Pd–Cl(1)	2.304(2)	Pd–Cl(2)	2.283(2)
Pd–P(1)	2.321(2)	Pd–P(2)	2.320(2)
P(1)–C(8)	1.844(9)	P(1)–C(21)	1.816(8)
P(1)–C(31)	1.817(8)	N(1)–C(1)	1.33(1)
N(1)–C(5)	1.33(1)	N(2)–C(6)	1.35(1)
N(2)–C(10)	1.34(1)	N(3)–C(11)	1.35(1)
N(3)–C(15)	1.35(1)	P(2)–C(58)	1.836(9)
P(2)–C(71)	1.833(8)	P(2)–C(81)	1.819(8)
N(51)–C(51)	1.35(1)	N(51)–C(55)	1.33(1)
N(52)–C(56)	1.33(1)	N(52)–C(60)	1.35(1)
N(53)–C(61)	1.35(1)	N(53)–C(65)	1.36(1)
Cl(1)–Pd–P(1)	87.45(7)	Cl(1)–Pd–P(2)	86.74(7)
Cl(2)–Pd–P(1)	92.66(8)	Cl(2)–Pd–P(2)	93.15(7)
Pd–P(1)–C(8)	116.7(3)	Pd–P(1)–C(21)	114.5(3)
Pd–P(1)–C(31)	109.8(2)	Pd–P(2)–C(58)	116.1(3)
Pd–P(2)–C(71)	115.2(2)	Pd–P(2)–C(81)	108.3(3)
C(8)–P(1)–C(31)	104.3(3)	C(21)–P(1)–C(31)	109.1(4)
C(8)–P(1)–C(21)	101.8(4)	C(58)–P(2)–C(71)	102.9(4)
C(58)–P(2)–C(81)	105.8(4)	C(71)–P(2)–C(81)	107.9(4)
C(1)–N(1)–C(5)	116.8(7)	N(1)–C(1)–C(2)	125.3(8)
N(1)–C(5)–C(4)	122.8(7)	N(1)–C(5)–C(6)	116.5(7)
C(6)–N(2)–C(10)	117.2(7)	C(5)–C(6)–N(2)	115.7(7)
N(2)–C(6)–C(7)	122.5(7)	P(1)–C(8)–C(7)	123.6(6)
P(1)–C(8)–C(9)	117.9(6)		

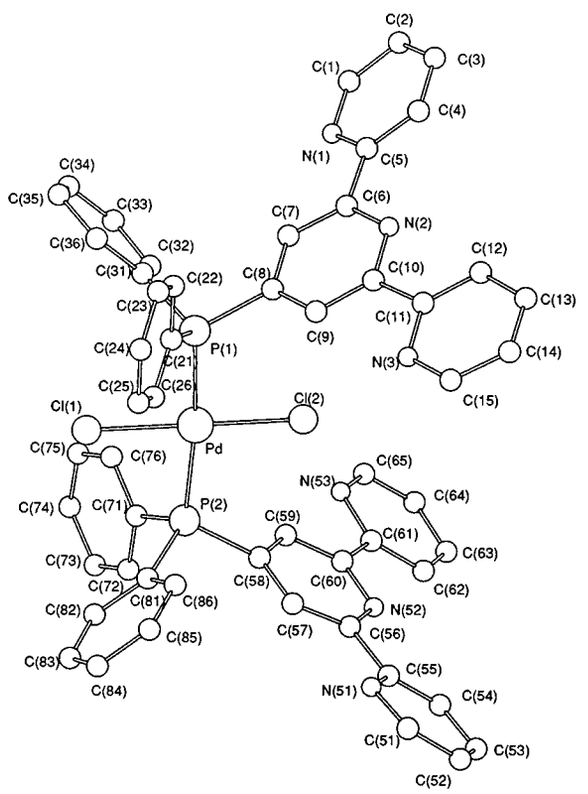


Fig. 5 Molecular structure of *trans*-$[PdCl_2L^1_2]$ determined for $[PdCl_2L^1_2]\cdot 2CH_2Cl_2$

Crystal structure of *trans*-$[PdCl_2L^1_2]\cdot 2.5CH_2Cl_2$

Yellow needles of $[PdCl_2L^1_2]\cdot 2.5CH_2Cl_2$ were obtained by diffusion of pentane into a dichloromethane solution. The molecular structure of *trans*-$[PdCl_2L^1_2]$ is shown in Fig. 5 and selected bond distances and angles are listed in Table 2. The

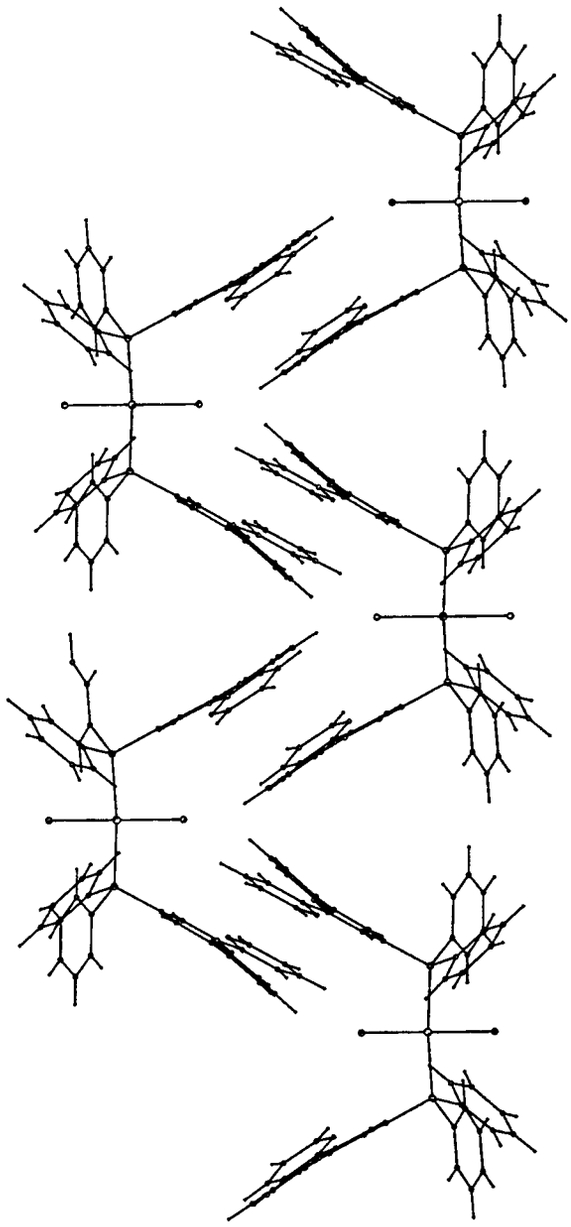


Fig. 6 Packing diagram for *trans*-$[PdCl_2L^1_2]\cdot 2CH_2Cl_2$ (solvate omitted) showing the interleaving of the terpyridine domains between adjacent molecules

palladium(II) centre is square planar as expected and the structural determination confirms a *trans* arrangement of the ligands with typical Pd–Cl and Pd–P bond distances. The two 4′-(diphenylphosphino)-2,2′:6′,2″-terpyridine ligands are oriented such that they face one another across one of the Pd–Cl bonds rather than adopting a paddle-wheel arrangement with respect to the metal centre. The bond parameters for the terpyridine units are unexceptional, and the nitrogen atoms of each unit adopt a *trans*,*trans* conformation as is typical for terpyridine ligands in which the *N*,*N*′,*N*″-donor set is uncoordinated.[33,36] Each terpyridine unit is essentially planar, with the root-mean-square deviations from planarity for each unit being 0.166 and 0.194 Å respectively. The torsion angles N(1)–C(5)–C(6)–N(2), N(2)–C(10)–C(11)–N(3), N(51)–C(55)–C(56)–N(52) and N(52)–C(60)–C(61)–N(53) are 11.9, 0.7, 11.6 and 3.7° respectively. The C_{terpy}–P–Pd bond angles are greater [92.66(8) and 93.15(7)°] than the C_{Ph}–P–Pd angles [87.45(7) and 86.74(7)°]. This may be due to the significant steric bulk of the terpyridine ligands, or may be a result of crystal-packing effects. Fig. 6 shows that, in the solid-state lattice, molecules of *trans*-$[PdCl_2L^1_2]$ are arranged so that the terpyridine domains of adjacent molecules are interleaved forming stacks.

The complex *trans*-$[PdCl_2L^1_2]$ is itself a difunctionalised terpyridine ligand, being a metallogue of a linear dinucleating phosphine and the chemistry of this and related compounds is presently being explored.

Conclusion

We have reported the synthesis of a new terpyridine ligand which bears a pendant diphenylphosphine group in the 4′ position. Our studies of its reactivity have demonstrated that, by using an appropriate metal centre, co-ordination may be through either the *P*- or *N*,*N*′,*N*″-donor sets. The potential for co-ordination through *both* donor groups provides us with the next stage in our investigations, namely the stepwise assembly of supramolecules.

Acknowledgements

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