The Palladium(II) Coordination Chemistry of Ferrocenylphosphinobipyridines: a Novel *trans*-Chelating Ligand System

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The reaction of dichloro(cycloocta-1,5-diene)palladium(II) with 1-diphenyl-(L^1) or 1-phenyl(*n*-butyl)-phosphino-1′-[6-(2,2′-bipyridyl)]ferrocene (L^2) results in the novel *trans*-coordination geometry with the β-pyridinyl ring and the phosphine group binding to the metal centre, as proved by a crystal structure determination of $[PdCl_2L^1][PdCl_2(cod)]$.

The coordination chemistry of phosphinoferrocenes, in particular the bis-phosphines such as bis(diphenylphosphino)ferrocene, bdppf[1–3] and aminophosphines such as α-*N*,*N*′-dimethylaminoethyl-2-diphenylphosphinoferrocene,[4–6] PPFA has been studied in great detail over the past 20 years because the resultant complexes often find synthetic applications in transition metal catalysed processes. Structural modifications have been made in both these ligand classes which result in families of sterically and electronically 'tunable' ligands. Less attention has been paid to related phosphinoferrocenes which do not possess a second phosphorus-centre or an amino group which could be used for chelation studies.

The synthesis of the related mixed phosphinobipyridylferrocenes has recently been described, however, no coordination chemistry of these compounds has been reported;[7] the actual synthesis is relatively straightforward using 1,1′-ferrocenediylphenylphosphine[8] as a precursor in a one-step reaction. The coordination chemistry of 6-ferrocenyl-2,2′-bipyridine,[9] a related derivative lacking the phosphine group, has been studied using palladium(II) from $[Pd(cod)Cl_2]$ and results in the metallation of the ferrocene in addition to the coordination of both nitrogen atoms with the formation of the complex **1**. The phosphinobipyridine compounds L^1 and L^2 would be expected to show different coordination modes with palladium(II) since three potential donor atoms are available, in addition to the possibility of metallation. However, *a priori* it is difficult to predict the coordination mode to be adopted by palladium with the only available knowledge being the anticipated square planar coordination of the metal.

The coordination experiments were carried out for L^1 and L^2 initially and the reaction in each case was followed *in situ* using NMR and CV. The ^{1}H NMR spectrum on addition of palladium indicates the rotation of the β-pyridinyl ring from the favoured conformation in the free ligand which is indicative of coordination of this ring.† This is accompanied by the coordination of the phosphorus atom as witnessed by the large downfield shift in the ^{31}P NMR spectrum (δ −27.59 to +22.63 for L^1 and −28.96 to +18.47 in L^2). Also on coordination of the ligands L^1 and L^2 there is an apparent cathodic shift in the $E_{\frac{1}{2}}$ values of the oxidation potentials of the ferrocene centres from 487 and 449 mV, respectively, to 434 and 377 mV (Fig. 1), however, because in the free ligands oxidation of the phosphorus precedes the ferrocene oxidation (E_{ox} phosphorus: 300 and 247 mV, respectively for L^1 and L^2) the shifts are not indicative of coordination polarisations of the ligands.

The latter result also indicates that no metallation occurs since this would involve a more significant cathodic shift (for example on metallation of 6-ferrocenyl-2,2′-bipyridine there is a cathodic shift of *ca.* 100 mV). Isolation of single crystals of reasonable quality for X-ray structural characterisation proved difficult, however, it was possible to isolate crystals of $[PdCl_2L^1]$ from a solution containing excess $[Pd(cod)Cl_2]$ which resulted in the cocrystallisation of the desired complex with $[Pd(cod)Cl_2]$. This was structurally characterised‡ and a SNOOPI drawing of the complex is shown in Fig. 2. It can be seen that in $[PdCl_2L^1]$ the coordination mode adopted by palladium is the unusual *trans*-coordination mode which is the first of its kind, to our knowledge, in monoferrocene ligand coordination chemistry. The square plane shows a slight

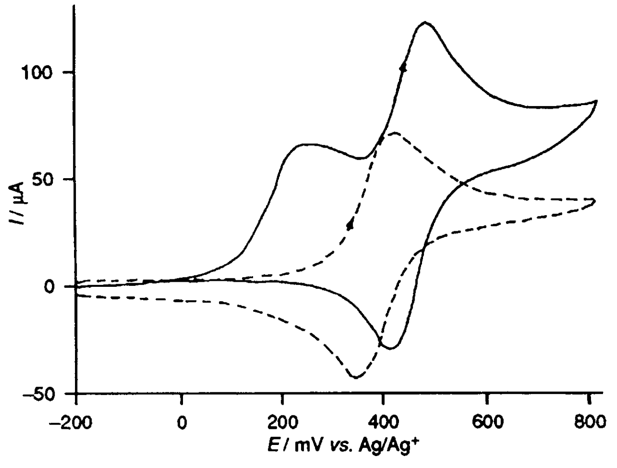


Fig. 1 CV of compound L^2 (10 mmol solution) (—) and after addition of an equimolar quantity of $[Pd(cod)Cl_2]$ (---) in 0.1 mol dm^{-3} tetra-*n*-butylammonium tetrafluoroborate in acetonitrile at a sweep rate of 100 mV s^{-1}

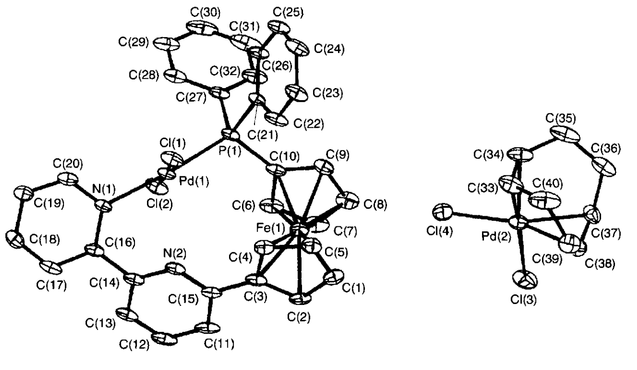
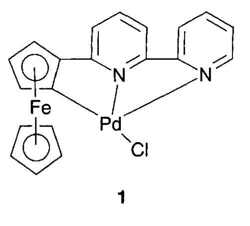


Fig. 2 Structure of $[PdCl_2L^1][Pd(cod)Cl_2]$. Important distances and angles: Pd(1)–Cl(1) 2.315(1), Pd(1)–Cl(2) 2.322(1), Pd(1)–P(1) 2.235(1), Pd(1)–N(1) 2.126(4), Pd(2)–Cl(3) 2.310(1), Pd(2)–Cl(4) 2.309(2), Pd(2)–C(33) 2.208(5), Pd(2)–C(34) 2.191(5), Pd(2)–C(37) 2.206(5), Pd(2)–C(38) 2.198(5)Å; Cl(1)–Pd(1)–Cl(2) 176.09(4), N(1)–Pd(1)–P(1) 173.92(10)°.



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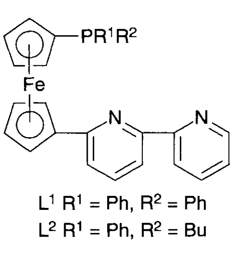

L^1 R^1 = Ph, R^2 = Ph
L^2 R^1 = Ph, R^2 = Bu

tetrahedral distortion with Pd(1) 0.077 Å out of the N(1)P(1)Cl(1)Cl(3) mean plane, probably caused by the steric requirement of the *trans* coordination of L^1. It is interesting to note that the second nitrogen is directed towards the metal centre [Pd(1)···N(2) 2.805(5) Å] and not in the lower energy *anti*-conformation as might be expected based solely on the interactions between the two pyridinyl rings. The two pyridinyl rings are mutually rotated by 32.1(1)°, again as a probable consequence of the short Pd(1)···N(2) contact. The phosphorus and nitrogen atoms of the β-pyridinyl ring form a pocket of perfect dimensions into which the palladium atom is accommodated [N(1)···P(1) 4.354(6) Å]. The dimensions of the $Fe(C_5H_4)_2$ moiety are normal [Fe–C 2.034–2.061(5) Å] with the two C_5H_5 rings almost eclipsed and parallel within 5.3(2)°.

The formation of these complexes opens up new areas of chemistry, for example, the formation of new extended structures by exchange of the halide ligands, or the possibility of extension into octahedral coordination with a range of transition metals in which a maximum of only two such ligands could coordinate. In addition, useful information in catalytic chemistry may be obtained because the *trans*-coordination may preclude normal oxidative addition reactions usually associated with palladium(II) catalysis. These avenues of research are currently being explored.

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Footnotes

† $[PdCl_2L^1]$: ^1H NMR ($CDCl_3$): δ 4.50 (m, 2H), 4.66 (m, 2H), 5.65 (2m, 4H), 7.30–7.95 (m's, 16H), $\{H\}^{31}P$: δ +22.63; $[PdCl_2L^2]$: ^1H NMR ($CDCl_3$): δ 0.80 (t, 3H), 1.20–1.50 (2m, 3H), 1.70–2.00 (m's, 2H), 2.86 (m, 1H), 4.36 (m, 1H), 4.43 (m, 1H), 4.50 (m, 1H), 4.63 (m, 1H), 4.68 (m, 1H), 4.80 (m, 1H), 5.00 (m, 1H), 6.72 (m, 1H), $\{H\}^{31}P$: δ 18.47 (from − 28.96 in free ligand). Satisfactory elemental analyses were obtained in both cases.

‡ *Crystal data* for $[PdCl_2L^1][PdCl_2(\underline{cod})]$: $[PdCl_2(C_{32}H_{25}FeN_2P)][PdCl_2(C_8H_{12})]$, $M = 987.14$, Triclinic, $P\bar{1}$, $a = 10.196(3)$, $b = 13.731(2)$, $c = 15.660(2)$ Å, $\alpha = 115.77(2)$, $\beta = 104.62(1)$, $\gamma = 93.29(2)°$, $U = 1875.0(7)$ Å^3, $Z = 2$, $D_c = 1.748$ g cm^{-3}, μ(Mo-Kα) = 16.91 cm^{-1}, $F(000) = 984$, $T = 150$ K.

All crystallographic measurements were made using a FAST area detector diffractometer and Mo-Kα radiation (λ = 0.71069 Å), following previously described procedures.[10] The structure was solved by direct methods (SHELX-S)[11] and refined on F_o^2 by full-matrix least-squares analysis (SHELXL-93)[12] using all 5200 unique data to final wR (on F^2) = 0.0912 and R (on F) = 0.0406 (hydrogens in idealised positions with U_{iso} freely refined, others anisotripic, 488 parameters). Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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