Preparation of 1,1'-Bis[(diphenylphosphino)methyl]ferrocene and its Transition-metal Complexes

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1,1'-Bis[(diphenylphosphino)methyl]ferrocene (dpmf), prepared from 1,1'-bis(chloromethyl)ferrocene and $LiPPh_2$, reacted with $[PdCl_2(MeCN)_2]$ to give $[Pd_2Cl_2(dpmf)_2]$ **1**, and treatment of **1** with $[Pd_3(2,6\text{-}Me_2C_6H_3NC)_6]$ in a 1:0.66 ratio in the presence of NH_4PF_6 and $2,6\text{-}Me_2C_6H_3NC$ produced a macrocyclic complex $[Pd_4(2,6\text{-}Me_2C_6H_3NC)_8(dpmf)_2]^{4+}$.

1,1'-Bis(diphenylphosphino)ferrocene (dppf) is rigid in its manner of co-ordination because of the direct binding of the phosphorus atoms to the cyclopentadienyl rings, and often forms chelated complexes.[1] In ruthenium and osmium clusters with dppf and the related 1,1'-bis(phosphino)ferrocene bridging bonding modes have been observed, but there are relatively few examples.[2] 1,1'-Bis[(diphenylphosphino)methyl]ferrocene (dpmf) formed by introduction of a methylene group between the cyclopentadienyl ring and phosphorus atom is less rigid than dppf and has the possibility of various co-ordination modes except chelation. We report here preparation of this new phosphine and its reactions with metal complexes.

1,1'-Bis[(diphenylphosphino)methyl]ferrocene (dpmf) was prepared in 72% yield by the reaction of 1,1'-bis(chloromethyl)ferrocene[3] (12 mmol) with lithium diphenylphosphide (24 mmol) in tetrahydrofuran (50 cm^3), followed by chromatography and recrystallization from benzene–hexane. The ^1H NMR spectrum showed a singlet at δ 3.14 due to methylene protons and two triplets at δ 3.84 and 3.92 due to cyclopentadienyl protons; couplings of the methylene protons with phosphorus atoms were not observed. The structure was confirmed by an X-ray analysis (Fig. 1).† The molecule has centrosymmetry at the iron atom. The P ··· P distance is 9.61 Å. When rotation of the cyclopentadienyl rings occurs the closest distance between the two P atoms becomes *ca.* 6.8 Å. On co-ordination chelation would be impossible, in contrast to dppf. However, the flexibility of the cyclopentadienyl rings provides a variety of potential co-ordination modes.

The cyclic voltammogram of a 0.5 mmol dm^{-3} solution of dpmf in 0.1 mol dm^{-3} $MeCN\text{-}CH_2Cl_2$ (1:1) containing NBu_4ClO_4 is quasi-reversible and showed a half-wave potential ($E_{\frac{1}{2}}$) at −0.05 V (*vs.* ferrocene–ferrocenium), ion scan rate 0.2 V s^{-1}. For comparison dppf showed a redox potential at 0.19 V. The

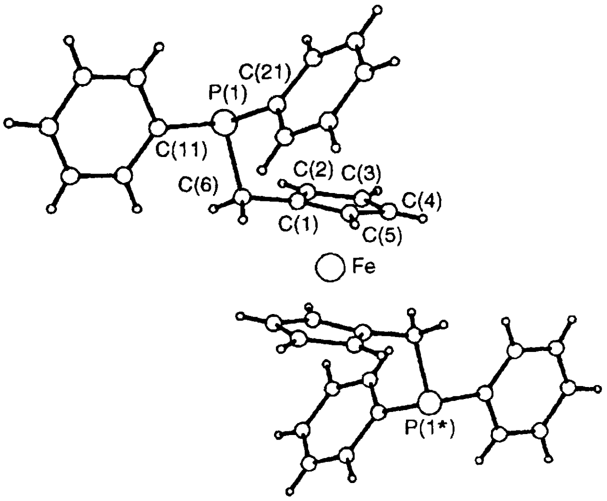

Fig. 1 Crystal structure of dpmf. Average bond distance: $Fe\text{–}C_5H_4$ 2.037(4) Å

CH_2PPh_2 group may have a greater electron-donating ability than that of the PPh_2 group. Methyl iodide when added to dpmf gave a phosphonium salt, $[Fe(C_5H_4CH_2PMePh_2)_2]$ quantitatively, similar to the reactivity of tertiary phosphines: ^1H NMR ($CDCl_3$), δ 2.49 (d, J_{PH} 7.2, 2CH_3), 3.97, 4.53 (s, C_5H_4, 8 H), 5.26 (d, J_{PH} 7.0 Hz, 2CH_2) and 7.5–8.0 (m, aromatic protons).

When dpmf (0.52 mmol) was treated with $[PdCl_2(MeCN)_2]$ (0.52 mmol) in CH_2Cl_2 (50 cm^3) orange crystals formulated as $[PdCl_2(dpmf)]\cdot 1.5CH_2Cl_2$ were isolated in a 61% yield and recrystallized from CH_2Cl_2 and diethyl ether: ^1H NMR ($CDCl_3$), δ 3.84–3.93 (m, CH_2 and C_5H_4, 12 H), 5.27 (s, CH_2Cl_2) and 7.20–7.63 (m, aromatic protons); UV/VIS (CH_2Cl_2), λ_{max} 338 nm (log ε 4.42). It was confirmed by an X-ray analysis that the complex exists as two independent molecules (**1a** and **1b**) in the unit cell and consists of a dimeric structure $[\{PdCl_2(dpmf)\}_2]\cdot 3CH_2Cl_2$ (Fig. 2).‡ The two

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† Crystal data: $C_{36}H_{32}FeP_2$, *M* = 582.4, monoclinic, space group $P2_1/n$ (no. 14), *a* = 9.905(2), *b* = 11.900(2), *c* = 12.656(2) Å, β = 98.37(1)°, *U* = 1475.9(4) $Å^3$, *Z* = 2, *F*(000) = 608, λ = 0.71073 Å, μ(Mo-Kα) = 6.39 cm^{-1}, D_c = 1.311 g cm^{-3}. Data were collected on a Rigaku AFC5S diffractometer in the range 3 < 2θ < 50° (2902 reflections collected, 2738 independent). The structure was solved by direct methods and refined by full-matrix least-squares techniques (non-hydrogen atoms refined anisotropically and hydrogen atoms included in calculated positions) to *R* = 0.037, *R'* = 0.032 for 1675 unique reflections [$I > 3\sigma(I)$]. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

‡ Crystal data: $C_{75}H_{70}Cl_{10}Fe_2P_4Pd_2\cdot 3CH_2Cl_2$, *M* = 1774.3, triclinic, space group $P\bar{1}$ (no. 2), *a* = 5.827(2), *b* = 19.592(2), *c* = 13.441(2) Å, α = 105.47(1), β = 102.69(1)°, γ = 100.62(1)°, *U* = 3785.6(9) $Å^3$, *Z* = 2, *F*(000) = 1788, μ(Mo-Kα) = 13.2 cm^{-1}, D_c = 1.556 g cm^{-3}. Of 13318 independent reflections (13847 collected), 3399 [$I > 3\sigma(I)$] were used for calculations, which were carried out in a similar manner to those for dpmf; *R* = 0.067, *R'* = 0.044.

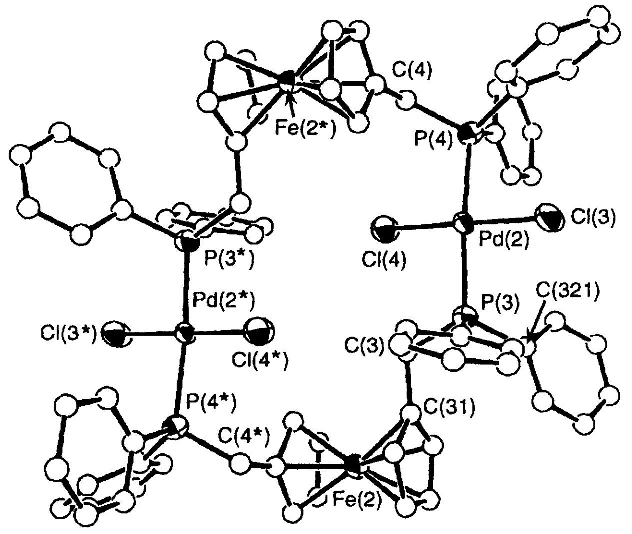
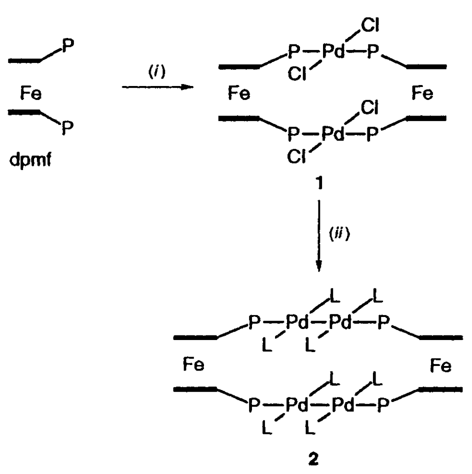


Fig. 2 Crystal structure of molecule **1b** showing the atom numbering scheme. Selected bond distances (Å) and angles (°): **1a**, Pd(1)–Cl(1) 2.281(5), Pd(1)–Cl(2) 2.305(6), Pd(1)–P(1) 2.320(7), Pd(1)–P(2) 2.342(7); Cl(1)–Pd(1)–Cl(2) 177.9(3), Cl(1)–Pd(1)–P(1), 87.6(2), Cl(1)–Pd(1)–P(2) 91.8(2), Cl(2)–Pd(1)–P(1) 92.3(2), Cl(2)–Pd(1)–P(2) 88.5(2), P(1)–Pd(1)–P(2) 175.9(3); **1b** Pd(2)–P(3) 2.330(7), Pd(2)–P(4) 2.339(7), Pd(2)–Cl(3) 2.289(6), Pd(2)–Cl(4) 2.303(6); Cl(3)–Pd(2)–Cl(4) 179.3(2), Cl(3)–Pd(2)–P(3) 86.2(2), Cl(3)–Pd(2)–P(4) 91.3(2), Cl(4)–Pd(2)–P(3) 93.2(2), Cl(4)–Pd(2)–P(4) 89.2(2), P(3)–Pd(2)–P(4) 174.4(3)

molecules have different ring structures. In **1a** the distance between the two palladium atoms is 8.08 Å and that between two phosphorus atoms is 7.32 Å, whereas these distances in **1b** are 7.32 and 7.50 Å, respectively. Torsion angles [C(2)-C(21)Fe(1)C(11) for **1a** and C(3)C(31)Fe(2)C(4) for **1b**] are −59 and −47°, respectively. These results suggest the existence of some flexibility in co-ordination mode. The bridged structure of the dpmf complex **1** is in contrast to that of the monomeric dppf complex [$PdCl_2$(dppf)] which has a chelated structure.[4] The reddish violet nickel complex [{$NiCl_2$(dmpf)}$_2$] was also prepared by the reaction of $NiCl_2 \cdot 2H_2O$ (0.42 mmol) with dpmf (0.50 mmol) in CH_2Cl_2 (40 cm^3). It is assumed to have a similar structure to that of **1**.

Reaction of complex **1** (0.20 mmol) with 2–3 equivalents of [Pd_3(2,6-$Me_2C_6H_3NC)_6$] in CH_2Cl_2 (10 cm^3) for 18 h at ambient temperature in the presence of NH_4PF_6 (2.0 mmol) and 2,6-$Me_2C_6H_3NC$ followed by crystallization from CH_2Cl_2 and ether produced an orange solid **2** formulated as [{Pd_2(2,6-$Me_2C_6H_3NC)_4$(dpmf)}$_2$][$PF_6]_4 \cdot CH_2Cl_2$ in 85% yield. The infrared spectrum showed a band at 2160 cm^{-1} and the ^1H NMR spectrum showed two singlets at δ 1.92 and 3.23, due to *o*-methyl and methylene protons, respectively. The ^{13}C NMR spectrum showed bands at δ 19.2, 30.7, 69.9, 71.3 and 81.2, the first assignable to *o*-methyl groups, the second to the methylene groups and the other three to the cyclopentadienyl groups. The carbon of terminal isocyanide appeared at δ 142.5. The UV/VIS spectrum in CH_2Cl_2 showed a band at λ_{max} 404 nm (log ε 4.20) due to the σ–σ* transition, resembling that of [Pd_2(2,6-$Me_2C_6H_3NC)_4(PPh_3)_2][PF_6]_2$ having a metal–metal bond.[5] Based on the spectroscopic data and the crystal structure of **1**, compound **2** is assumed to have a macrocyclic structure containing four palladium atoms, as depicted in Scheme 1.



Scheme 1 Reactions of dpmf, L = 2,6-$Me_2C_6H_3NC$. (*i*) [$PdCl_2$-$(MeCN)_2$]; (*ii*) 2–3 equivalents [Pd_3L_6], NH_4PF_6

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