



Synthesis, coordination studies and redox properties of a novel ditertiary phosphine bearing two ferrocenyl groups

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ABSTRACT

The new ferrocenyl substituted ditertiary phosphine $\{FcCH_2N(CH_2PPh_2)CH_2\}_2$ [$Fc = (\eta^5-C_5H_4)Fe(\eta^5-C_5H_5)$] (**1**) was prepared, in 72% yield, by Mannich based condensation of the known bis secondary amine $\{FcCH_2N(H)CH_2\}_2$ with 2 equiv. of Pb_2PCH_2OH in CH_3OH . Phosphine **1** readily coordinates to various transition-metal centres including Mo^0 , Ru^{II} , Rh^I , Pd^{II} , Pt^{II} and Au^I to afford the heterometallic complexes $\{RuCl_2(p-cym)\}_2$ (**2**), $(AuCl)_2$ (**3**), *cis*- $PtCl_2$ (**4**), *cis*- $PdCl_2$ (**5**), *cis*- $Mo(CO)_4$ (**6**), *trans,trans*- $\{Pd(CH_3)Cl\}_2$ (**7**) and *trans,trans*- $\{Rh(CO)Cl\}_2$ (**8**). In complexes **2**, **3**, **7** and **8** ligand **1** displays a *P,P'*-bridging mode whilst for **4–6** a *P,P'*-chelating mode is observed. All new compounds have been fully characterised by spectroscopic and analytical methods. Furthermore the structures of **1**, **2** · $2CH_2Cl_2$, **3** · CH_2Cl_2 , **4** · CH_2Cl_2 , **6** · $0.5CHCl_3$ and **8** have been elucidated by single crystal X-ray crystallography. Electrochemical measurements have been undertaken, and their redox chemistry discussed, on both non-complexed ligand **1** and representative compounds containing this new ditertiary phosphine.

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1. Introduction

The ferrocenyl (Fc) group continues to play a fundamental role in the design of new mono- and polyphosphorus containing ligands and some of their transition metal complexes have been studied as homogenous catalysts [1–5]. The versatility of the Fc group in synthesis can be illustrated by some of the diverse compounds (Chart 1) previously documented in the literature. The Fc group can be employed either as a substituent bonded to phosphorus [6] or a metal centre [7] through an ethynyl linker or alternatively as a backbone for accessing primary and secondary phosphines [8], di- and polyphosphines [9,10], nonsymmetric ligands [11–14] and chiral systems [15–18]. To date, 1,1'-bis(diphenylphosphino)ferrocene (dppf) possibly remains the most iconic example of a phosphorus(III) based ligand containing the Fc moiety [4,19–23]. Furthermore the ferrocenyl group continues to attract much attention because of the redox active metal centre present, thereby allowing studies of electronic communication for the development of new electronic materials and devices [24–26]. Recently Tucker and co-workers have shown how ferrocenyl modified ureas can be used as enantioselective electrochemical sensors for chiral carboxylates [27].

We report here the synthesis of a new ditertiary phosphine bearing two pendant ferrocenyl groups and a brief survey of its coordination chemistry to Mo^0 , Ru^{II} , Rh^I , Pd^{II} , Pt^{II} and Au^I metal centres. The electrochemical properties of the non complexed li-

gand and selected compounds is reported along with six single crystal X-ray structure determinations.

2. Experimental

2.1. Materials

Standard Schlenk techniques were used for the synthesis of **1** whilst all other reactions were carried out in air using previously distilled solvents unless otherwise stated. Diphenylphosphino-methanol has been reported elsewhere [28] and the metal precursors $\{RuCl_2(p-cym)\}_2$ (*p-cym* = *p-cymene*) [29], $AuCl(tht)$ (*tht* = tetrahydrothiophene) [30], $MCl_2(cod)$ (*M* = Pd, Pt, *cod* = cycloocta-1,5-diene) [31], $Pd(CH_3)Cl(cod)$ [32] and $Mo(CO)_4$ (*nbd*) (*nbd* = norbornadiene) [33] prepared according to known procedures. The secondary amine $\{FcCH_2N(H)CH_2\}_2$ was prepared following slight modification of a known method [34b] whilst all other chemicals were obtained from commercial sources and used directly without further purification.

2.2. Instrumentation

Infrared spectra were recorded as KBr pellets in the range $4000–200\text{ cm}^{-1}$ on a Perkin–Elmer System 2000 Fourier-transform spectrometer, 1H NMR spectra (400 MHz) on a Bruker DPX-400 FT spectrometer with chemical shifts (δ) in ppm to high frequency of $Si(CH_3)_4$ and coupling constants (*J*) in Hz, $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DPX-400 FT spectrometer with

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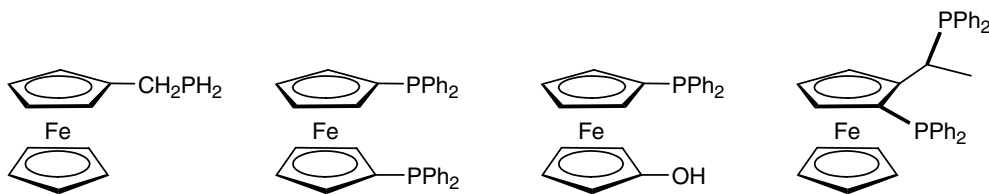


Chart 1.

chemical shifts (δ) in ppm to high frequency of 85% H_3PO_4 . All NMR spectra were measured in CDCl_3 unless otherwise stated. Elemental analyses (Perkin–Elmer 2400 CHN or Exeter Analytical, Inc. CE-440 Elemental Analyzers) were performed by the Loughborough University Analytical Service within the Department of Chemistry.

2.3. Syntheses

2.3.1. $\{\text{FcCH}_2\text{N}(\text{CH}_2\text{PPh}_2)\text{CH}_2\}_2$ (**1**)

Under a nitrogen atmosphere, an orange suspension of $\{\text{FcCH}_2\text{N}(\text{H})\text{CH}_2\}_2$ (0.496 g, 1.087 mmol) and $\text{Ph}_2\text{PCH}_2\text{OH}$ (0.495 g, 2.175 mmol) in methanol (HPLC grade, 20 mL) was stirred at room temperature for 72 h. The yellow suspension was concentrated under reduced pressure to approximately 10 mL and the solid filtered and dried under reduced pressure. Yield: 0.663 g, 72%. Selected data for **1**: $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): -27.3 ppm. ^1H NMR: δ 7.35–7.21 (m, 20H, arom. H), 4.01 (m, 4H, C_5H_4), 4.00 (m, 4H, C_5H_4), 3.99 (s, 10H, C_5H_5), 3.54 (s, 4H, CH_2NH), 3.11 (d, 4H, $^2J_{\text{PH}}$ 3.6 Hz, CH_2P), 2.58 (s, 4H, $\text{CH}_2\text{C}_5\text{H}_4$). FAB-MS: m/z 667 [M–PPh₂]. Anal. Calc. for $\text{C}_{50}\text{H}_{50}\text{N}_2\text{Fe}_2\text{P}_2 \cdot 0.75\text{H}_2\text{O}$ (866.11) requires: C, 69.35; H, 6.00; N, 3.25. Found: C, 69.25; H, 5.95; N, 3.35%.

2.3.2. $\{\text{RuCl}_2(p\text{-cym})\}_2\{\text{FcCH}_2\text{N}(\text{CH}_2\text{PPh}_2)\text{CH}_2\}_2$ (**2**)

Compound **1** (0.038 g, 0.043 mmol) was added to a stirred solution of $\{\text{RuCl}(\mu\text{-Cl})(p\text{-cym})\}_2$ (0.026 g, 0.043 mmol) in CH_2Cl_2 (20 mL). The resulting solution was stirred for 0.5 h before concentrating the solvent under reduced pressure to approximately 2 mL. Hexane (25 mL) was added and the resulting orange suspension stirred for a further 0.5 h. The orange precipitate was filtered and dried under reduced pressure. Yield: 0.054 g, 86%. Selected data for **2**: $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): 25.2 ppm. ^1H NMR: δ 7.94–7.46 (m, 20 H, arom. H), 5.37 (s, 4H, CH_2NH), 5.20 (d, 4H, $^3J_{\text{HH}}$ 5.2 Hz, CH), 5.12 (d, 4H, $^3J_{\text{HH}}$ 6 Hz, CH), 3.99 (t, 4H, C_5H_4), 3.88 (s, 10H, C_5H_5), 3.74 (t, 4H, C_5H_4), 3.64 (d, 4H, $^2J_{\text{PH}}$ 2.8 Hz, CH_2P), 2.52 (s, 4H, $\text{CH}_2\text{C}_5\text{H}_4$), 2.39 (sept, $^3J_{\text{HH}}$ 7 Hz, 2H, CH), 1.79 (s, 6H, CH_3), 0.96 (d, 12H, $^3J_{\text{HH}}$ 6.8 Hz, CH_3). FAB-MS: m/z 973 [M– $\text{RuCl}_2(p\text{-cym})\text{PPh}_2$]. Anal. Calc. for $\text{C}_{78}\text{H}_{78}\text{N}_2\text{Fe}_2\text{P}_2\text{Cl}_4\text{Ru}_2 \cdot \text{CH}_2\text{Cl}_2$ (1550.03) requires: C, 55.00; H, 5.20; N, 1.80. Found: C, 54.95; H, 5.25; N, 2.15%.

2.3.3. $\{\text{AuCl}\}_2\{\text{FcCH}_2\text{N}(\text{CH}_2\text{PPh}_2)\text{CH}_2\}_2$ (**3**)

Compound **1** (0.108 g, 0.118 mmol) was added to a stirred solution of $\text{AuCl}(\text{tht})$ (0.076 g, 0.236 mmol) in CH_2Cl_2 (20 mL). The resulting solution was stirred in the dark for 0.5 h and concentrated under reduced pressure to approx. 2 mL. Hexane (25 mL) was added and the resulting yellow suspension stirred for a further 0.5 h. The yellow precipitate was filtered and dried under reduced pressure. Yield: 0.130 g, 84%. Selected data for **3**: $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): 19.4 ppm. ^1H NMR: δ 7.68–7.40 (m, 20H, arom. H), 4.03 (m, 18H, C_5H_4 and C_5H_5), 3.64 (d, 4H, $^2J_{\text{PH}}$ 1.2 Hz, CH_2P), 3.51 (s, 4H, CH_2NH), 2.60 (s, 4H, $\text{CH}_2\text{C}_5\text{H}_4$). FT-IR (KBr): ν_{AuCl} 330 cm^{-1} . FAB-MS: m/z 1317 [M]. Anal. Calc. for $\text{C}_{50}\text{H}_{50}\text{N}_2\text{Fe}_2\text{P}_2\text{Au}_2\text{Cl}_2$ (1317.47) requires: C, 45.60; H, 3.85; N, 2.15. Found: C, 45.45; H, 3.85; N, 2.00%.

2.3.4. $\text{cis-PtCl}_2\{\text{FcCH}_2\text{N}(\text{CH}_2\text{PPh}_2)\text{CH}_2\}_2$ (**4**)

Compound **1** (0.075 g, 0.088 mmol) was added to a stirred solution of $\text{PtCl}_2(\text{cod})$ (0.033 g, 0.087 mmol) in CH_2Cl_2 (20 mL). The solu-

tion was stirred for 0.5 h and the solvent concentrated to ca. 2 mL under reduced pressure. Diethyl ether (25 mL) was added and the resulting yellow suspension stirred for a further 0.5 h. The yellow precipitate was filtered and dried under reduced pressure. Yield: 0.085 g, 86%. Selected data for **4**: $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): 2.60 ppm, $^1J(\text{PtP})$ 3666 Hz. ^1H NMR: δ 7.60–7.20 (m, 20H, arom. H), 4.11 (m, 4H, C_5H_4), 4.01 (s, 10H, C_5H_5), 3.98 (m, 4H, C_5H_4), 3.76 (s, 4H, $^3J_{\text{PH}}$ 33.1 Hz, CH_2P), 3.09 (s, 4H, CH_2NH), 3.02 (s, 4H, $\text{CH}_2\text{C}_5\text{H}_4$). FT-IR (KBr): ν_{PtCl} 318 and 294 cm^{-1} . FAB-MS: m/z 1118 [M]. Anal. Calc. for $\text{C}_{50}\text{H}_{50}\text{N}_2\text{Fe}_2\text{P}_2\text{Cl}_2\text{Pt} \cdot 2.5\text{H}_2\text{O}$ (1163.64) requires: C, 51.60; H, 4.75; N, 2.40. Found: C, 51.65; H, 4.60; N, 2.30%.

2.3.5. $\text{PdCl}_2\{\text{FcCH}_2\text{N}(\text{CH}_2\text{PPh}_2)\text{CH}_2\}_2$ (**5**)

Compound **1** (0.011 g, 0.124 mmol) was added to a stirred solution of $\text{PdCl}_2(\text{cod})$ (0.034 g, 0.117 mmol) in CH_2Cl_2 (20 mL). The solution was stirred for 0.5 h and the solvent concentrated to ca. 2 mL under reduced pressure. Diethyl ether (25 mL) was added and the resulting cream suspension stirred for a further 0.5 h. The cream precipitate was filtered and dried under reduced pressure. Yield: 0.089 g. Attempts to obtain an analytically pure sample of **5** were hampered by slow decomposition in solution.

2.3.6. $\text{cis-Mo}(\text{CO})_4\{\text{FcCH}_2\text{N}(\text{CH}_2\text{PPh}_2)\text{CH}_2\}_2$ (**6**)

Compound **1** (0.096 g, 0.107 mmol) and $\text{Mo}(\text{CO})_4(\text{ncd})$ (0.032 g, 0.107 mmol) in degassed CH_2Cl_2 (10 mL) were stirred at ambient temperature for ca. 10 d under a nitrogen atmosphere. The solvent was concentrated to approx. 2 mL under reduced pressure. Diethyl ether (25 mL) was added and the resulting orange suspension stirred for a further 0.5 h. The orange precipitate was filtered and dried under reduced pressure. Yield: 0.065 g, 58%. Selected data for **6**: $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): 29.0 ppm. ^1H NMR: δ 7.44–7.32 (m, 20H, arom. H), 3.99 (m, 4H, C_5H_4), 3.85 (m, 14H, C_5H_4 and C_5H_5), 3.29 (s, 4H, CH_2), 2.78 (s, 4H, CH_2), 1.97 (s, 4H, CH_2). FT-IR (KBr): ν_{CO} 2018, 1918, 1898, 1870 cm^{-1} . FAB-MS: m/z 1061 [M]. Anal. Calc. for $\text{C}_{54}\text{H}_{50}\text{N}_2\text{O}_4\text{Fe}_2\text{P}_2\text{Mo} \cdot 1.75\text{CH}_2\text{Cl}_2$ (1209.28) requires: C, 55.37; H, 4.46; N, 2.32. Found: C, 55.40; H, 4.25; N, 2.45%.

2.3.7. $\text{Trans,trans-Pd}(\text{CH}_3)\text{Cl}\{\text{FcCH}_2\text{N}(\text{CH}_2\text{PPh}_2)\text{CH}_2\}_2$ (**7**)

Compound **1** (0.111 g, 0.121 mmol) was added to a stirred solution of $\text{Pd}(\text{CH}_3)\text{Cl}(\text{cod})$ (0.032 g, 0.121 mmol) in CH_2Cl_2 (20 mL). The solution was stirred for 0.5 h and the solvent concentrated to approx. 2 mL under reduced pressure. Hexane (25 mL) was added and the resulting cream suspension stirred for a further 0.5 h. The cream precipitate was filtered and dried under reduced pressure. Yield: 0.074 g, 61%. Selected data for **7**: $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): 13.0 ppm. ^1H NMR: δ 7.83–7.33 (m, 20H, arom. H), 4.29 (t, 4H, C_5H_4), 4.24 (t, 4H, C_5H_4), 4.20 (s, 10H, C_5H_5), 3.81 (s, 4H, CH_2), 3.67 (s, 4H, CH_2), 3.59 (br, 4H, CH_2), 0.00 (t, 3H, $^3J_{\text{PH}}$ 12 Hz, CH_3). FT-IR (KBr): ν_{PdCl} 262 cm^{-1} . FAB-MS: m/z 973 [M–Cl]. Anal. Calc. for $\text{C}_{51}\text{H}_{53}\text{N}_2\text{Fe}_2\text{P}_2\text{ClPd} \cdot 2.5\text{H}_2\text{O}$ (1054.56) requires: C, 58.10; H, 5.05; N, 2.65. Found: C, 58.05; H, 5.10; N, 2.70%.

2.3.8. $\text{Trans,trans-Rh}(\text{CO})\text{Cl}\{\text{FcCH}_2\text{N}(\text{CH}_2\text{PPh}_2)\text{CH}_2\}_2$ (**8**)

Compound **1** (0.098 g, 0.112 mmol) was added to a stirred solution of $\{\text{Rh}(\mu\text{-Cl})(\text{CO})_2\}_2$ (0.023 g, 0.056 mmol) in CH_2Cl_2 (20 mL). The solution was stirred for 0.5 h and the solvent concentrated to

ca. 2 mL under reduced pressure. Diethyl ether (25 mL) was added and the resulting orange suspension stirred for a further 0.5 h. The orange precipitate was filtered and dried under reduced pressure. Yield: 0.033 g, 29%. Selected data for **8**: $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): 16.6 ppm., $^1\text{J}(\text{RhP})$ 130 Hz. ^1H NMR: δ 7.73–7.29 (m, 20H, arom. H), 4.19 (t, 4H, C_5H_4), 4.16 (t, 4H, C_5H_4), 4.11 (s, 10H, C_5H_5), 3.94 (s, 4H, CH_2), 3.76 (s, 4H, CH_2), 3.57 (s, 4H, CH_2). FT-IR (KBr): ν_{CO} 1969 cm^{-1} . FAB-MS: m/z 983 [M–Cl]. Anal. Calc. for $\text{C}_{51}\text{H}_{50}\text{N}_2\text{O}-\text{Fe}_2\text{P}_2\text{ClRh} \cdot 1.25\text{H}_2\text{O}$ (1041.51) requires: C, 58.80; H, 5.10; N, 2.70. Found: C, 58.40; H, 4.80; N, 3.20%.

2.4. X-ray crystallography

Crystals of **1** and **6** were obtained by slow diffusion of CH_3OH into a CH_2Cl_2 solution. Suitable crystals of **2** and **3** were grown by vapour diffusion of hexane onto CH_2Cl_2 solutions. X-ray quality crystals of compounds **4** and **8** were obtained by slow evaporation of a $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ solution.

Details of the crystal data for **1**, **2**· $2\text{CH}_2\text{Cl}_2$, **3**· CH_2Cl_2 , **4**· CH_2Cl_2 , **6**· 0.5CHCl_3 and **8** along with a summary of data collection parameters are given in Table 1. Measurements for **2**· $2\text{CH}_2\text{Cl}_2$ and **4**· CH_2Cl_2 were made on a Bruker Apex 2 CCD diffractometer using graphite monochromated radiation from a sealed tube Mo K α source. For **1** and **8** silicon 111 monochromated synchrotron radiation at Daresbury Laboratory SRS station 9.8 on a Bruker Apex 2 CCD diffractometer. Diffraction data for **3**· CH_2Cl_2 and **6**· 0.5CHCl_3 was collected using a rotating anode source and a Bruker–Nonius 95 mm or Roper CCD camera. Narrow frame ω -scans were employed for **1**, **2**· $2\text{CH}_2\text{Cl}_2$, **4**· CH_2Cl_2 and **8**, θ and ω -scans were used for **3**· CH_2Cl_2 and **6**· 0.5CHCl_3 . Intensities were corrected semi-empirically for absorption, based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods (Patterson synthesis for **2**· $2\text{CH}_2\text{Cl}_2$ and **3**· CH_2Cl_2) and refined on F^2 values for all unique data by full-matrix least squares. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were constrained in a riding model with U_{eq} set to $1.2U_{\text{eq}}$ of the carrier atom ($1.5U_{\text{eq}}$ for methyl hydrogen). In **3**· CH_2Cl_2 and **4**· CH_2Cl_2 the CH_2Cl_2 molecule was modelled with the carbon and one chlorine disordered over two sets of positions; major occupancy = 59.2(9)% for **4**· CH_2Cl_2 and 70.9(5)% for **3**· CH_2Cl_2 . Programs used were COLLECT [35] or Bruker AXS APEX2 [36] for diffractometer control and DENZO or SAINT for frame integration [37,38], Bruker SHELXTL [39] for structure solution, refinement, and molecular graphics and local programs. Disordered molecules of CH_2Cl_2 (for **2**· $2\text{CH}_2\text{Cl}_2$) or CHCl_3 (for **6**· 0.5CHCl_3) were modelled by the Platon Squeeze procedure [40].

2.5. Electrochemistry

Cyclic voltammetric measurements were carried out on a EG&G Model PAR 263A potentiostat/galvanostat using a standard cell, consisting of a Pt disc working electrode ($d = 1.6$ mm), Ag/AgCl reference electrode in a 3 M NaCl solution and a Pt gauze counter electrode, at a scan rate of 50 mV/s. All measurements were performed at ambient temperature (22 ± 1 °C) in dry, degassed CH_2Cl_2 solutions containing analyte (0.001 M) and $[\text{NBu}_4][\text{BF}_4]$ (0.1 M) as the supporting electrolyte. Ferrocene was used as an internal standard.

Table 1a

Crystallographic data for **1**, **2**· $2\text{CH}_2\text{Cl}_2$ and **3**· CH_2Cl_2

| Compound | 1 | 2 · $2\text{CH}_2\text{Cl}_2$ | 3 · CH_2Cl_2 |
|--|---|---|--|
| Empirical formula | $\text{C}_{50}\text{H}_{50}\text{Fe}_2\text{N}_2\text{P}_2$ | $\text{C}_{70}\text{H}_{78}\text{Cl}_4\text{Fe}_2\text{N}_2\text{P}_2\text{Ru}_2 \cdot 2\text{CH}_2\text{Cl}_2$ | $\text{C}_{50}\text{H}_{50}\text{Au}_2\text{Cl}_2\text{Fe}_2\text{N}_2\text{P}_2 \cdot \text{CH}_2\text{Cl}_2$ |
| Formula weight | 852.56 | 1634.78 | 1402.32 |
| Crystal system | Triclinic | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| <i>a</i> (Å) | 7.6347(4) | 10.4845(4) | 11.9161(2) |
| <i>b</i> (Å) | 11.3939(5) | 12.6125(5) | 12.7979(2) |
| <i>c</i> (Å) | 12.7421(6) | 15.1788(7) | 17.2109(3) |
| α (°) | 95.6966(5) | 96.720(2) | 72.111(2) |
| β (°) | 103.7690(5) | 105.962(2) | 81.279(2) |
| γ (°) | 102.5657(5) | 106.968(2) | 80.243(2) |
| Volume (Å ³) | 1037.36(9) | 1802.81(13) | 2447.75(7) |
| <i>Z</i> | 1 | 1 | 2 |
| λ | 0.6710 | 0.71073 | 0.71073 |
| <i>T</i> (K) | 150(2) | 150(2) | 120(2) |
| D_{calc} (Mg/m ³) | 1.365 | 1.506 | 1.903 |
| Absorption coefficient (mm ⁻¹) | 0.814 | 1.188 | 6.877 |
| Crystal habit and colour | Lath; orange | Block; orange | Tablet; yellow |
| Crystal size (mm ³) | 0.19 × 0.04 × 0.03 | 0.40 × 0.28 × 0.11 | 0.18 × 0.08 × 0.04 |
| θ Range (°) | 1.75–31.02 | 1.99–30.56 | 3.00–27.54 |
| Reflections collected | 13 143 | 21 443 | 52 848 |
| Independent reflections | 6964 [0.0326] | 10 789 [0.0187] | 11 242 [0.0406] |
| Completeness (%) | 97.4 | 99.4 | 99.3 |
| Number of parameters | 253 | 373 | 588 |
| Final R^a , R_w^b | 0.036, 0.099 | 0.028, 0.072 | 0.028, 0.064 |

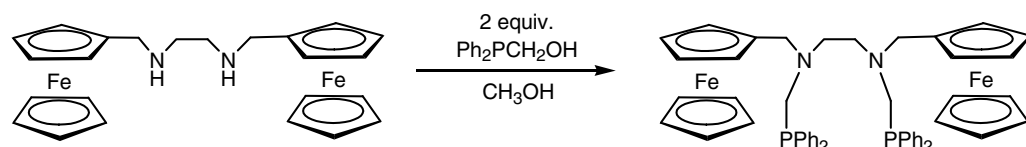
$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR_2 = \left[\frac{\sum [w(F_o^2 - F_c^2)]^2}{\sum [w(F_o^2)]^2} \right]^{1/2}$$

3. Results and discussion

3.1. Ligand synthesis

Ferrocenyl derived phosphines have been accessed through a number of established methods previously [1a,2,6,8,12,14]. In our work we have found that phosphorus based Mannich condensation reactions are extremely flexible procedures for preparing highly functionalised phosphines [41] and even nonsymmetric diphosphines [42] by employing two consecutive elimination steps. The new ditertiary phosphine **1** was synthesised in 72% yield by double condensation of the known bis secondary amine precursor $\{\text{FcCH}_2\text{N}(\text{H})\text{CH}_2\}_2$ [34] with 2 equiv. of $\text{Ph}_2\text{PCH}_2\text{OH}$ in CH_3OH at ambient temperature (Eq. (1)). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed one new phosphorus resonance at $\delta(\text{P}) -27.3$ ppm, some 20 ppm upfield from that observed for the starting compound $\text{Ph}_2\text{PCH}_2\text{OH}$. Compound **1** showed no evidence for oxidation when CDCl_3 solutions were left to stand for ca. 6 d. The ^1H NMR spectrum showed all the characteristic resonances expected for **1** and, furthermore, the absence of a ν_{NH} stretch in the FT-IR spectrum confirmed the ternary nature of both nitrogen atoms.



(1)

3.2. Coordination studies

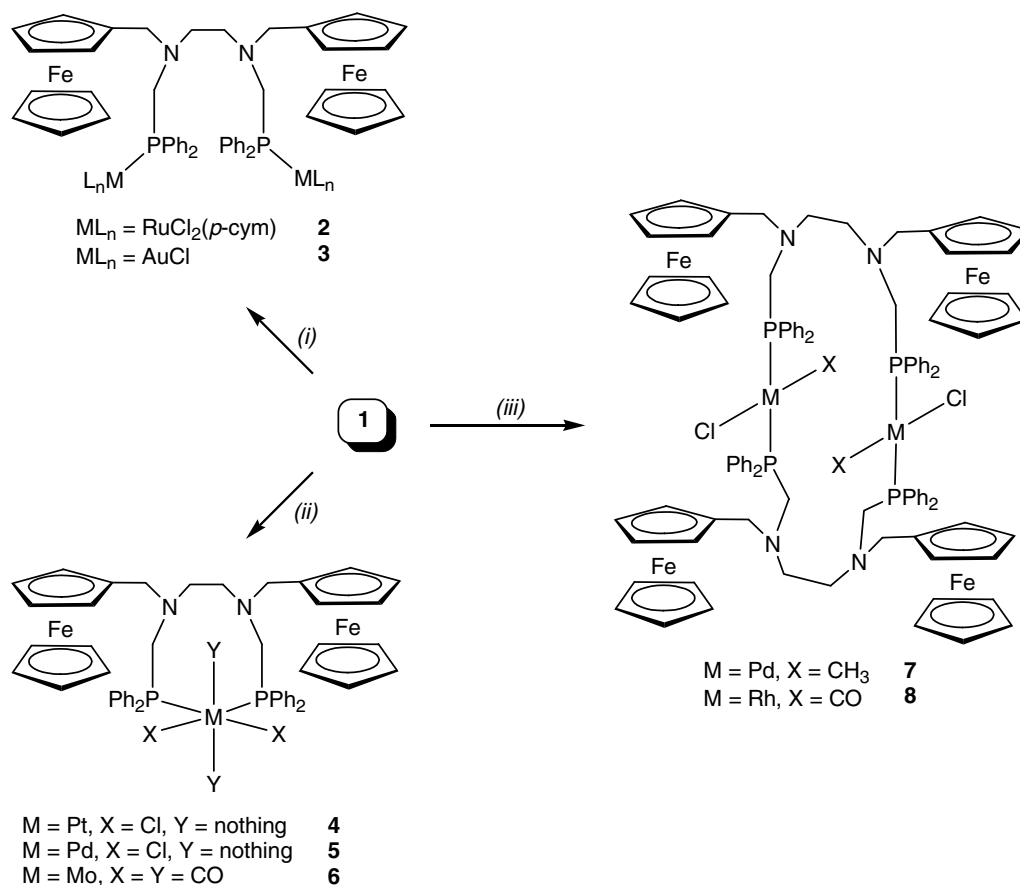
Complexation of the metalloligand **1** to various transition metal centres was explored in order to understand the ligating modes of this new ferrocenyl ditertiary phosphine. The diphosphine dppf is known to preferentially act either in a η^2 -chelating fashion or *P,P*-bridging mode [3]. Treatment of $\{\text{RuCl}(\mu\text{-Cl})(p\text{-cym})\}_2$ (1 equiv.) or $\text{AuCl}(\text{tht})$ (2 equiv.) with **1** in dichloromethane at ambient temperature gave the tetrametallic complexes $\{\text{RuCl}_2(p\text{-cym})\}_2\{\text{FcCH}_2\text{N}(\text{CH}_2\text{PPh}_2)\text{CH}_2\}_2$ (**2**) and $\{\text{AuCl}\}_2\{\text{FcCH}_2\text{N}(\text{CH}_2\text{PPh}_2)\text{CH}_2\}_2$ (**3**), respectively (Scheme 1). In both complexes diphosphine **1** bridges either $\{\text{RuCl}_2(p\text{-cym})\}$ or AuCl metal fragments. Displacement of *cod* from $\text{PtCl}_2(\text{cod})$ with 1 equiv. of **1** in dichloromethane gave the new square-planar trimetallic complexes *cis*- $\text{PtCl}_2(\mathbf{1})$ (**4**). In contrast, reaction of **1** with either $\text{PdCl}_2(\text{cod})$ or $\text{PdCl}_2(\text{PhCN})_2$ gave an impure sample of *cis*- $\text{PdCl}_2(\mathbf{1})$ (**5**) which, by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy in solution, revealed the presence of several phosphorus containing species [$\delta(\text{P})$ 20.8 ppm, 11.1 ppm], the major being assigned to either *cis*- or *trans*-isomers of $\text{PdCl}_2(\mathbf{1})$ (possibly monomeric or dimeric). Careful monitoring of CDCl_3 , CD_2Cl_2 or C_6D_6 solutions over a period of four days revealed the gradual disappearance of these signals and two new doublets at significant downfield shifts [$\delta(\text{P})$ 159.9 ppm, 79.1 ppm, $^2J_{\text{PP}}$ 17 Hz]. This in conjunction with the observation of a new doublet at $\delta(\text{H})$ 3.06 ppm ($^2J_{\text{HP}}$ 39 Hz) in the ^1H NMR spectrum led us to speculate that **5** undergoes slow decomposition to give the five-membered chelate complex $[\text{PdCl}_2(\text{Ph}_2\text{PCH}_2\text{OPPh}_2)]$ with elimination of some hitherto unidentified ferrocenylamine byproducts. Support for the nonsymmetric nature of this coordinated bidentate phosphorus(III) ligand comes from previous studies with $\text{Ph}_2\text{PCH}_2\text{OPPh}_2$ [43] and, more recently, $\text{RR}'\text{POCH}_2\text{P-}$

$(\text{CH}_2\text{OH})_2$ ($\text{R}, \text{R}' = \text{Ph}, \text{Cy}$) [44]. With **4** this transformation is very slow as would be expected for the different reactivity between $\text{Pd}(\text{II})$ and $\text{Pt}(\text{II})$ square-planar metal centres. The octahedral *cis*-tetracarbonylmolybdenum(0) complex **6** was prepared from $\text{Mo}(\text{CO})_4(\text{nbd})$ and one equiv. of **1** in dichloromethane. Further characterising details for compounds **2–6** are given in the Experimental Section.

Reaction of **1** with $\text{Pd}(\text{CH}_3\text{Cl})(\text{cod})$ in dichloromethane gave *trans,trans*- $\{\text{Pd}(\text{CH}_3\text{Cl})(\mathbf{1})\}_2$ (**7**). In **7**, we believe the diphosphine **1** functions as a bridging ligand on the basis of the spectroscopic data obtained. A further example of this ligand behaviour is seen in the analogous chlorocarbonylrhodium(I) complex **8** prepared from $\{\text{Rh}(\mu\text{-Cl})(\text{CO})_2\}_2$ and 2 equiv. of **1**. A *trans* disposition of $-\text{PPh}_2$ groups was inferred by a sharp doublet at $\delta(\text{P})$ 16.6 ppm ($^1J_{\text{RhP}}$ 130 Hz) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum and the geometry accountable on the basis of the large spacer separation between both phosphorus(III) groups. However a dimeric species with a *trans,trans*- $\{\text{Rh}(\text{CO})\text{Cl}\}$ fragment disposition has been proposed [45] for $\{\{\text{RhCl}(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}\}_2$ ($n = 1, 3$ or 4) and, on the basis of FT-IR data for **8** [ν_{CO} 1969 cm^{-1}], this geometry would be anticipated for **8** and similarly for the dipalladium(II) complex **7**. The X-ray structure (vide infra) for **8** has been determined and confirms the dimeric nature. In contrast FAB-MS data on the bulk sample showed only a significant monomeric $[\text{M}-\text{Cl}]$ ion at m/z 983 whereas MALDI analysis gave unreliable results.

3.3. Single crystal X-ray studies

The single crystal X-ray structures of the free ligand **1** and five illustrative complexes **2** · $2\text{CH}_2\text{Cl}_2$, **3** · CH_2Cl_2 , **4** · CH_2Cl_2 , **6** · 0.5CHCl_3 and **8** have each been determined with selected bond



Scheme 1. (i) $\{\text{RuCl}(\mu\text{-Cl})(p\text{-cym})\}_2$ or $\text{AuCl}(\text{tht})$, CH_2Cl_2 ; (ii) $\text{MCl}_2(\text{cod})$, CH_2Cl_2 or $\text{Mo}(\text{CO})_4(\text{nbd})$, CH_2Cl_2 ; (iii) $\text{Pd}(\text{CH}_3\text{Cl})(\text{cod})$ or $\{\text{Rh}(\mu\text{-Cl})(\text{CO})_2\}_2$, CH_2Cl_2 .

Table 1b
Crystallographic data for **4** · CH₂Cl₂, **6** · 0.5CHCl₃ and **8**

| Compound | 4 · CH ₂ Cl ₂ | 6 · 0.5CHCl ₃ | 8 |
|--|--|--|--|
| Empirical formula | C ₅₀ H ₅₀ Cl ₂ Fe ₂ N ₂ P ₂ Pt · CH ₂ Cl ₂ | C ₅₄ H ₅₀ Fe ₂ N ₂ O ₄ P ₂ Mo · 0.5CHCl ₃ | C ₁₀₂ H ₁₀₀ Cl ₂ Fe ₄ N ₄ O ₂ P ₄ Rh ₂ |
| Formula weight | 1203.48 | 1120.22 | 2037.86 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | <i>P2</i> ₁ / <i>n</i> | <i>P2</i> ₁ / <i>n</i> | <i>P2</i> ₁ / <i>n</i> |
| <i>a</i> (Å) | 17.6469(17) | 18.1242(3) | 13.0780(10) |
| <i>b</i> (Å) | 12.6761(12) | 12.7301(2) | 20.4797(16) |
| <i>c</i> (Å) | 21.866(2) | 22.9350(3) | 17.3102(13) |
| α (°) | | | |
| β (°) | 104.448(2) | 109.4910(8) | 105.1038(11) |
| γ (°) | | | |
| Volume (Å ³) | 4736.6(8) | 4988.39(13) | 4476.1(6) |
| <i>Z</i> | 4 | 4 | 2 |
| λ | 0.71073 | 0.71073 | 0.6884 |
| <i>T</i> /K | 150(2) | 120(2) | 150(2) |
| <i>D</i> _{calc} [Mg/m ³] | 1.688 | 1.492 | 1.512 |
| Absorption coefficient (mm ⁻¹) | 3.882 | 1.014 | 1.176 |
| Crystal habit and colour | Block; yellow | Tablet; orange | Plate; yellow |
| Crystal size (mm ³) | 0.29 × 0.18 × 0.11 | 0.26 × 0.09 × 0.05 | 0.07 × 0.04 × 0.02 |
| θ Range (°) | 1.71–28.34 | 2.91–27.48 | 1.52–29.50 |
| Reflections collected | 47747 | 53164 | 51962 |
| Independent reflections [<i>R</i> _{int}] | 11782 [0.0867] | 11463 [0.0500] | 13698 [0.0895] |
| Completeness (%) | 99.9 | 99.8 | 99.9 |
| Number of parameters | 578 | 587 | 541 |
| Final <i>R</i> ^a , <i>Rw</i> ^b | 0.049, 0.119 | 0.043, 0.121 | 0.049, 0.117 |

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

lengths and angles given in Tables 2 and 3. The molecular structure of **1** (Fig. 1) confirms that the phosphorus atoms are in a pyramidal

geometry as indicated by the relevant C–P–C angles. Both phosphorus atoms lie in an anti conformation with respect to each

Table 2
Selected bond distances (Å) and angles (°) for compounds **1**, **2** · 2CH₂Cl₂, **3** · CH₂Cl₂, **4** · CH₂Cl₂ and **8**

| | 1 | 2 · 2CH ₂ Cl ₂ (M = Ru) | 3 · CH ₂ Cl ₂ (M = Au) | 4 · CH ₂ Cl ₂ (M = Pt) | 8 (M = Rh) |
|--------------------------|------------|--|---|---|------------------------|
| Fe(1)–Cp _{cent} | 1.6426(6) | 1.6423(8) | 1.644(2), 1.655(2) | 1.654(3) | 1.6426(17), 1.6415(19) |
| Fe(2)–Cp _{cent} | 1.6455(6) | 1.6417(9) | 1.653(2), 1.652(2) | 1.649(3) | 1.6456(16), 1.6495(18) |
| P(1)–C(13) | 1.8922(12) | 1.8575(15) | 1.851(4) | 1.871(6) | 1.845(3) |
| C(13)–N(1) | 1.4573(15) | 1.4560(19) | 1.469(5) | 1.456(7) | 1.458(4) |
| N(1)–C(14) | 1.4721(15) | 1.473(2) | 1.486(5) | 1.472(7) | 1.470(4) |
| N(1)–C(25) | 1.4653(15) | 1.460(2) | 1.470(5) | 1.484(7) | 1.476(4) |
| C(25)–C(25') | 1.522(2) | 1.521(3) | | | |
| C(25)–C(26) | | | 1.524(5) | 1.509(8) | 1.516(4) |
| C(26)–N(2) | | | 1.475(5) | 1.485(7) | 1.475(4) |
| N(2)–C(27) | | | 1.477(5) | 1.492(7) | 1.470(4) |
| N(2)–C(38) | | | 1.467(5) | 1.468(7) | 1.451(4) |
| C(38)–P(2) | | | 1.848(4) | 1.853(6) | 1.859(3) |
| Ru–Cym _{cent} | | 1.6929(7) | | | |
| M(1)–Cl(1) | | 2.4088(4) | 2.2836(10) | 2.3535(14) | 2.3739(9) |
| M(1)–Cl(2) | | 2.4173(4) | | 2.3558(15) | |
| M(1)–P(1) | | 2.3448(4) | 2.2277(9) | 2.2551(15) | 2.3063(9) |
| M(1)–P(2) | | | | 2.2401(14) | 2.3130(9) |
| Pt(1)–H(26A) | | | | 2.49 | |
| Rh(1)–C(51) | | | | | 1.809(4) |
| C(51)–O(1) | | | | | 1.148(4) |
| P(1)–C(13)–N(1) | 115.74(8) | 114.40(10) | 109.5(3) | 113.3(4) | 115.6(2) |
| C(13)–N(1)–C(14) | 110.69(9) | 111.07(12) | 112.5(3) | 110.3(4) | 112.9(2) |
| C(13)–N(1)–C(25) | 112.97(9) | 112.15(13) | 111.0(3) | 113.3(4) | 113.1(3) |
| N(1)–C(25)–C(25') | 110.95(12) | 111.29(17) | | | |
| N(1)–C(25)–C(26) | | | 113.6(3) | 114.1(5) | 114.2(3) |
| C(25)–C(26)–N(2) | | | 109.8(3) | 113.5(4) | 108.8(3) |
| C(26)–N(2)–C(27) | | | 113.9(3) | 109.6(4) | 113.7(3) |
| C(26)–N(2)–C(38) | | | 113.7(3) | 112.7(4) | 114.7(2) |
| C(27)–N(2)–C(38) | | | 109.8(3) | 109.5(4) | 113.9(3) |
| N(2)–C(38)–P(2) | | | 109.3(3) | 112.8(4) | 106.4(2) |
| Cl(1)–M(1)–P(1) | | 85.276(14) | 178.53(4) | 84.71(5) | 90.13(3) |
| Cl(2)–M(1)–P(1) | | 83.435(14) | | 170.42(5) | |
| Cl(1)–M(1)–Cl(2) | | 88.397(14) | | 87.00(5) | |
| Cl(1)–M(1)–P(2) | | | | 166.34(5) | 85.31(3) |
| Cl(2)–M(1)–P(2) | | | | 84.71(5) | |
| P(1)–M(1)–P(2) | | | | 103.05(5) | 161.97(3) |
| C(51)–M(1)–P(1) | | | | | 90.17(11) |
| C(51)–M(1)–P(2) | | | | | 93.82(11) |
| C(51)–M(1)–Cl(1) | | | | | 178.02(12) |

Table 3
Selected bond distances (Å) and angles (°) for compound **6** · 0.5CHCl₃

| 6 · 0.5CHCl ₃ | |
|--------------------------|------------|
| Fe(1)–Cp _{cent} | 1.6516(15) |
| Fe(2)–Cp _{cent} | 1.6537(16) |
| P(1)–C(13) | 1.861(3) |
| C(13)–N(1) | 1.465(3) |
| N(1)–C(14) | 1.478(4) |
| N(1)–C(25) | 1.469(3) |
| C(25)–C(26) | 1.519(4) |
| C(26)–N(2) | 1.461(3) |
| N(2)–C(27) | 1.474(3) |
| N(2)–C(38) | 1.457(4) |
| C(38)–P(2) | 1.867(3) |
| Mo(1)–C(51) | 1.980(3) |
| Mo(1)–C(52) | 1.995(3) |
| Mo(1)–C(53) | 2.022(3) |
| Mo(1)–C(54) | 2.063(3) |
| Mo(1)–P(1) | 2.5416(7) |
| Mo(1)–P(2) | 2.5547(8) |
| P(1)–C(13)–N(1) | 112.55(18) |
| C(13)–N(1)–C(14) | 110.3(2) |
| C(13)–N(1)–C(25) | 111.2(2) |
| N(1)–C(25)–C(26) | 113.2(2) |
| C(25)–C(26)–N(2) | 113.8(2) |
| C(26)–N(2)–C(27) | 113.5(2) |
| C(26)–N(2)–C(38) | 112.3(2) |
| C(27)–N(2)–C(38) | 114.5(2) |
| N(2)–C(38)–P(2) | 111.43(18) |
| C(51)–Mo(1)–C(52) | 84.46(13) |
| C(51)–Mo(1)–C(53) | 87.94(13) |
| C(51)–Mo(1)–C(54) | 92.23(13) |
| C(52)–Mo(1)–C(53) | 90.09(13) |
| C(52)–Mo(1)–C(54) | 91.42(13) |
| C(53)–Mo(1)–C(54) | 178.49(12) |
| C(51)–Mo(1)–P(1) | 85.07(9) |
| C(51)–Mo(1)–P(2) | 172.82(9) |
| C(52)–Mo(1)–P(1) | 169.51(9) |
| C(52)–Mo(1)–P(2) | 88.61(9) |
| C(53)–Mo(1)–P(1) | 88.86(9) |
| C(53)–Mo(1)–P(2) | 90.21(9) |
| C(54)–Mo(1)–P(1) | 89.66(8) |
| C(54)–Mo(1)–P(2) | 89.81(8) |
| P(1)–Mo(1)–P(2) | 101.83(2) |

other (symmetry imposed) and the Fe···Fe separation is 11.181 Å. This separation could be important in promoting interactions between iron centres when investigating their electrochemical properties (*vide infra*). The two cyclopentadienyl rings of ferrocene are eclipsed and essentially coplanar (torsional twist about the Cp_{cent}···Fe···Cp_{cent} is 3.4°). Upon complexation to afford the tetrametallic complexes **2** · 2CH₂Cl₂ (Fig. 2) and **3** · CH₂Cl₂ (Fig. 3), there are minimal bond length or bond angle changes in the P–C–N–C–N–C–P saturated backbone (Table 2). In the piano-stool complex **2** · 2CH₂Cl₂, the Ru–Cl, Ru–P and Ru–C_{cent} distances are as expected [41b] and this trend is similarly observed for the linear gold(I) complex **3** · CH₂Cl₂ which shows typical metric parameters (Table 2) [46]. The Fe···Fe separation in **2** · 2CH₂Cl₂ is 10.187 Å which is significantly greater than that found in **3** · CH₂Cl₂ (6.794 Å) but slightly shorter than in non complexed **1** (11.181 Å). In **3** · CH₂Cl₂ there are no short intramolecular or intermolecular Au···Au separations often encountered in many examples of two-coordinate gold(I) phosphine complexes [41d]. However molecules of **3** · CH₂Cl₂ do associate (Fig. 4), via head-to-tail Au···Cl contacts [Cl(2)···Au(2')] 3.950 Å [47]. For **2** · 2CH₂Cl₂ the cyclopentadienyl rings of ferrocene are eclipsed and essentially coplanar [torsional twist about the Cp_{cent}···Fe···Cp_{cent} is 1.1° at Fe(1)] whilst for **2** · 2CH₂Cl₂ the torsion angles are larger [4.0° at Fe(1) and 21.9° at Fe(2)].

In the dichloroplatinum(II) compound **4** · CH₂Cl₂ (Fig. 5) the ligand **1** adopts a *cis* disposition around the square-planar plati-

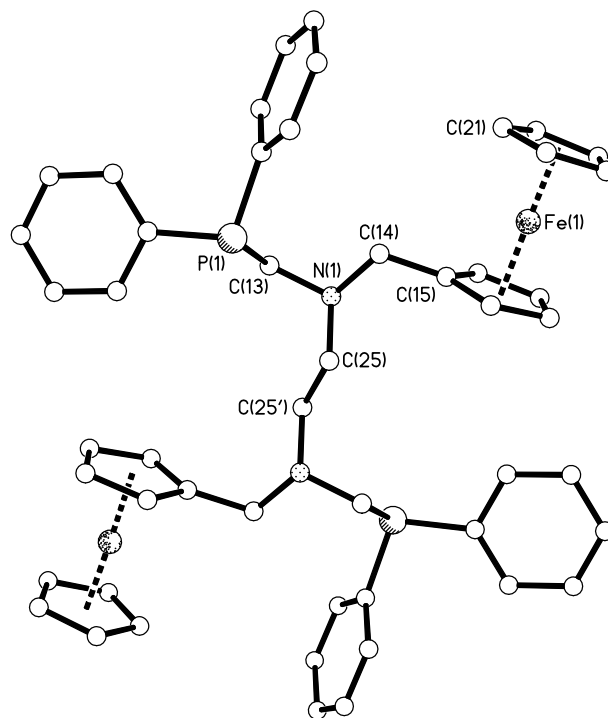


Fig. 1. X-ray structure of **1**. All hydrogens have been removed for clarity. Symmetry operator: ' = -x + 1, -y + 1, -z + 1.

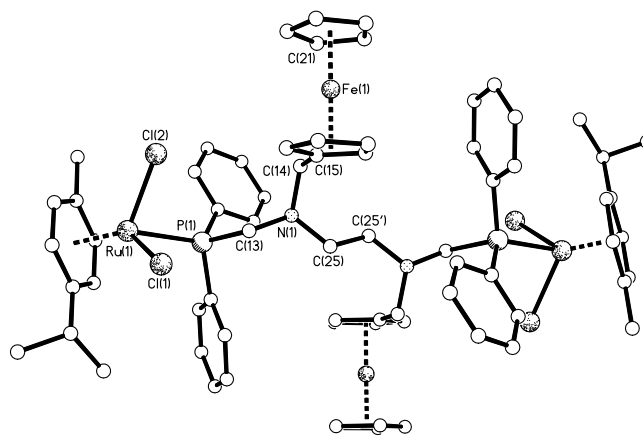


Fig. 2. X-ray structure of **2**. All hydrogens and solvent molecules have been removed for clarity. Symmetry operator: ' = -x + 1, -y + 1, -z + 1.

num(II) centre forming a nine-membered chelate ring. Upon inspection of the structural variations in the P–C–N–C–N–C–P backbone minimal changes are observed when **1** adopts a chelating mode of coordination. The Fe···Fe separation in **4** · CH₂Cl₂ is 6.510 Å which is shorter than that found in **2** · 2CH₂Cl₂, **3** · CH₂Cl₂ and noncomplexed **1**. A feature in **4** · CH₂Cl₂ that has been observed in other medium ring sized palladium(II) and platinum(II) complexes [48] is the close contact between H(26A) of coordinated **1** and the Pt centre [C(26)···Pt(1) 3.365 Å, H(26A)···Pt(1) 2.4871 Å, Pt(1)···H(26A)–C(26) 148°]. This axial interaction between the C_{sp³}-H bond of the ligand backbone and the platinum(II) centre is not significantly mirrored in the ¹H NMR spectrum of **4** in which there is only a small downfield shift (ca. Δδ 0.6 ppm). The two cyclopentadienyl rings of both ferrocenes are eclipsed and essentially coplanar [torsional twist about the Cp_{cent}···Fe···Cp_{cent} is 1.6° at Fe(1) and 8.5° at Fe(2)]. The molecular structure of mono-

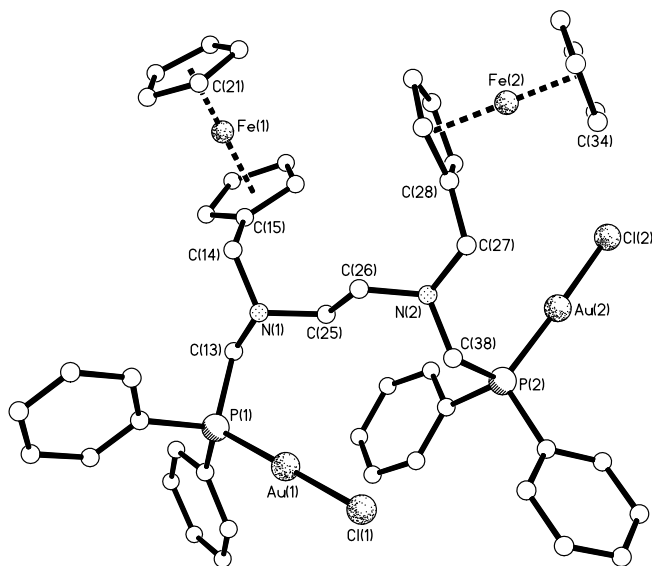


Fig. 3. X-ray structure of **3**. All hydrogens and solvent molecule have been removed for clarity.

meric **6** (Fig. 6, Table 3) comprises a *cis*-chelating **1** and four terminal CO ligands [vide infra for comparison with a related molybdenum(0) complex of *dpph* (*dpph* = 1,6-bis(diphenylphosphino)hexane) reported by Ueng and Hwang]. The Mo–P and Mo–C bond lengths are broadly as anticipated [49] and the P(1)–Mo(1)–P(2) angle similar to that found for **4**. In keeping with the structures of **1–4** discussed previously, the torsion twist angles about the $C_{P_{cent}} \cdots Fe \cdots C_{P_{cent}}$ in **6**·0.5CHCl₃ are 11.8° and 13.2° while the Fe···Fe separation is 7.040 Å.

The X-ray structure of **8** (Figs. 7 and 8, Table 2) shows that **1** bridges two *trans*-RhCl(CO) fragments with formation of a large 18-membered metallomacrocyclic ring. There is a crystallographic inversion centre lying at the centroid of the 18-membered ring. The P(1)–Rh(1)–P(2) angle deviates some 18° from the idealised angle for a *trans* disposition of groups. The torsion twist angles about the $C_{P_{cent}} \cdots Fe \cdots C_{P_{cent}}$ in **8** are 13.0° and 3.4° while the Fe···Fe separations are 6.987 Å [Fe(1)···Fe(2)], 13.511 Å [Fe(1)···Fe(1a)], 14.232 Å [Fe(1)···Fe(2a)] and 17.893 Å [Fe(2)···Fe(2a)]. Between adjacent *trans*-RhCl(CO) fragments the Rh···Rh separation is 6.199 Å and is considerably shorter than found in a related dimeric rhodium(I) complex containing a diphosphine ligand based on bisphenol [9.0005(11) Å] [50]. The structure of **8** represents the first crystallographically character-

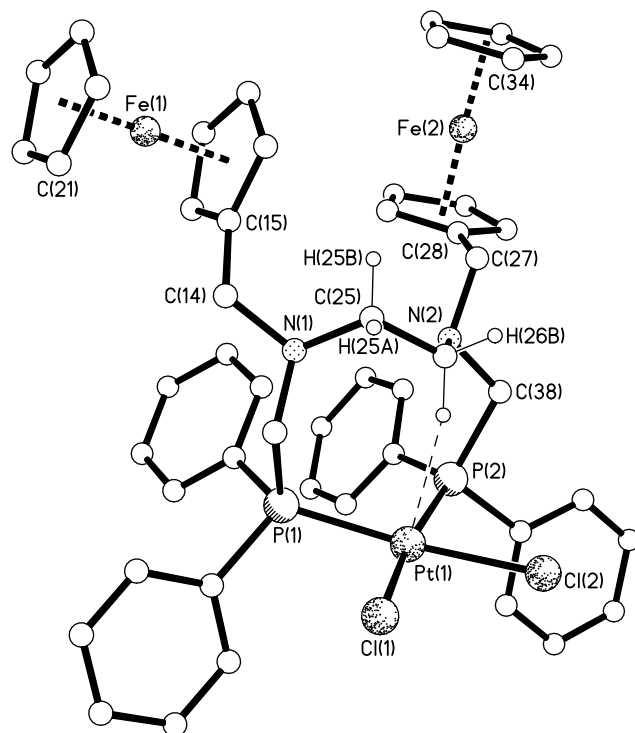


Fig. 5. X-ray structure of **4**. All hydrogens and solvent molecule have been removed for clarity.

ised metallacycle containing an Rh₂Fe₄ arrangement of metal centres. In comparison with the analogous ligand *dpph*, containing a C₆ carbon backbone, this bridging motif has been observed in several complexes with different metal fragments. Hence it has been shown that two *dpph* ligands can bridge a range of three- {Cu(OClO₃)} [51], four- (*trans*-PdCl₂ [52], tetrahedral CoCl₂ [53]) and six- (*trans*-Mo(CO)₄) [54] coordinate metal centres.

3.4. Electrochemical properties

The electrochemical behaviour of **1** and its related mononuclear and dinuclear complexes has been investigated by cyclic voltammetry and their half-wave redox potentials summarised in Table 4. All of the compounds studied were found to display a single reversible ferrocene/ferrocenium redox (Fc/Fc⁺) couple similar to that of ferrocene. For **1**, the half-wave potential of the Fc groups was found to be at $E_{1/2} +0.055$ V whereas for complexes **2**, **4**, **6**

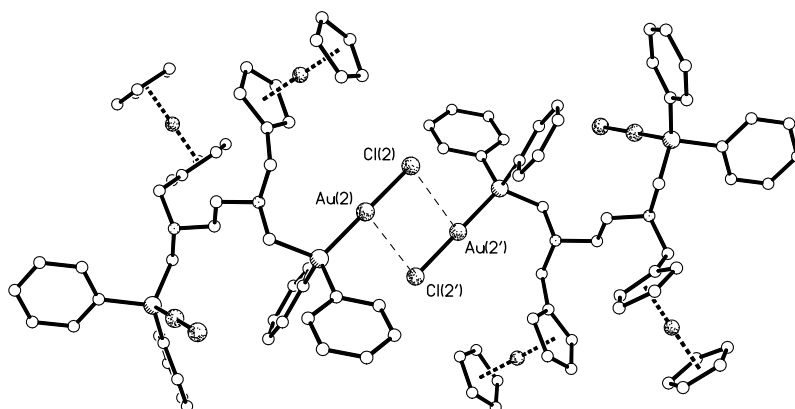


Fig. 4. X-ray structure of **3** showing the Au···Cl contacts between adjacent molecules. Symmetry operator: ' = $-x + 1, -y, -z + 1$

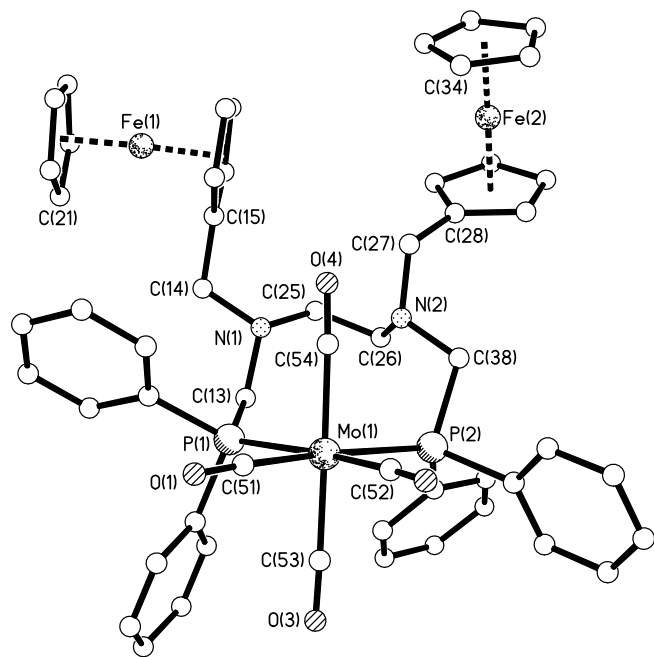


Fig. 6. X-ray structure of **6**. All hydrogens and solvent molecule have been removed for clarity.

and **7** the half potentials were observed in the range $E_{1/2}$ -0.018 to $+0.135$ V. The observation of a single Fc/Fc^+ wave for **1**, **2**, **6** and **7** indicates no direct or indirect electronic communication between the two ferrocene groups, i.e. no electronic interaction via (saturated) covalent bonds or any significant coulombic interaction through space, as the two ferrocene centres are spatially too far apart from each other. As a result both ferrocene centres are considered electrochemically equivalent and apparently undergo simultaneous oxidation. In contrast, the platinum(II) complex **4** displays a broad cyclic voltammogram suggesting that the two ferrocene/ferrocenium redox couples are marginally different.

The cyclic voltammogram of **1** is more complex showing two further irreversible oxidation potentials at $E_{1/2}$ -0.015 and

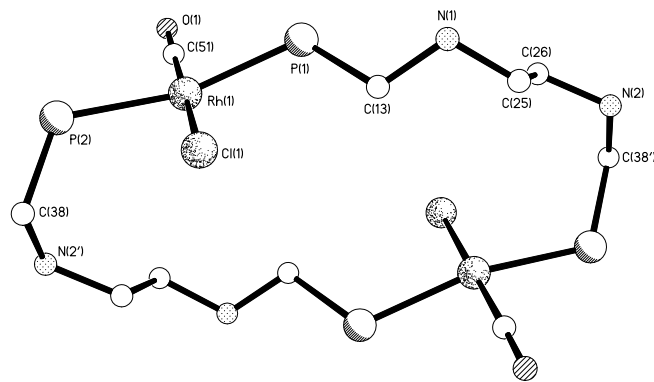


Fig. 8. X-ray structure of **8** showing the core arrangement of the metallomacrocycle.

Table 4
Electrochemical data^a for **1** and its mononuclear and dinuclear complexes **2–4**, **6** and **7**

| | $E_{1/2}$ (V) ^b , $Fe^{II/III}$ |
|----------|--|
| 1 | +0.055 |
| 2 | -0.018 |
| 3 | +0.012 |
| 4 | +0.075 |
| 6 | +0.135 |
| 7 | +0.021 |

^a All experiments were performed in a 0.1M $[NBu_4][BF_4]$ /dry CH_2Cl_2 solution at a scan rate of 50 mV s^{-1} .

^b $E_{1/2} = (E_{pc} + E_{pa})/2$ reported relative to the ferrocene/ferrocenium couple.

0.215 V (Fig. 9). These potentials are tentatively assigned to the irreversible oxidation of both tertiary phosphine centres in **1**, whilst the appearance at two potentials, one more cathodic than the other, suggests sequential electrochemical oxidation of **1**. In addition to the Fc/Fc^+ couple, the dinuclear ruthenium(II) complex **3** was found to exhibit a more complex cyclic voltammogram. This may tentatively result from two consecutive irreversible single-electron (per ruthenium atom) $Ru^{II} \rightarrow Ru^{III}$ oxidations [55,56]. Similarly complex **6** showed further irreversible oxidation potentials

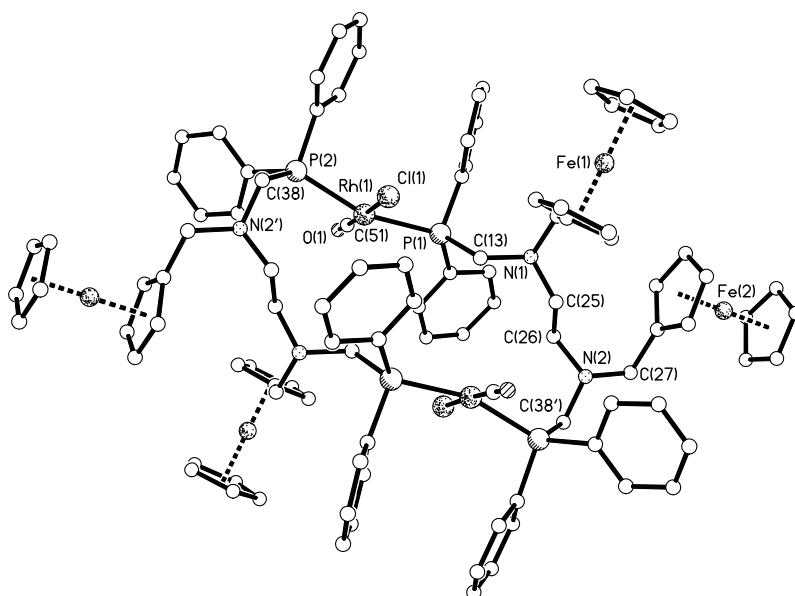


Fig. 7. X-ray structure of **8**. All hydrogens have been removed for clarity.

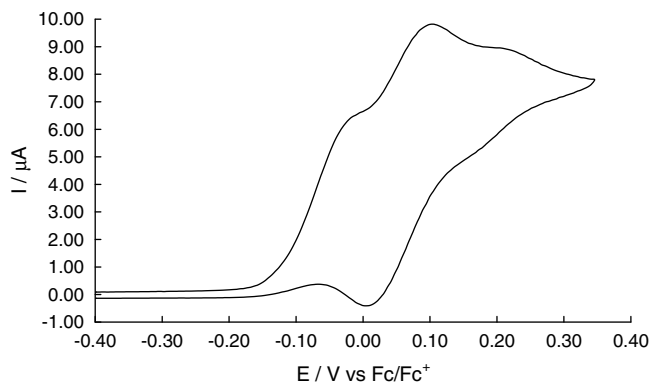


Fig. 9. Cyclic voltammogram of **1** in dry CH_2Cl_2 , 0.1 M $[\text{NBu}_4][\text{BF}_4]$ at a scan rate of 50 mV s^{-1} .

that presumably correspond to the $\text{Mo}^0 \rightarrow \text{Mo}^{\text{I}}$ and $\text{Mo}^{\text{I}} \rightarrow \text{Mo}^{\text{II}}$ oxidations respectively of the molybdenum tetracarbonyl fragment [9].

4. Conclusions

In summary, we have shown that a new ditertiary phosphine with ferrocenyl appendages, can be prepared and complexed to a range of soft transition metal centres. Coordination studies with **1** have shown that only P-donor atoms are used and no evidence was found for P,N-coordination involving the tertiary N-donor atoms [57,58]. The electrochemical properties of these compounds have been briefly investigated along with detailed X-ray crystallographic studies of six compounds. Further studies are in progress and will be reported in due course.

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Appendix A. Supplementary material

CCDC 676678, 676679, 676680, 676681, 676682, and 676683 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.04.005](https://doi.org/10.1016/j.jorganchem.2008.04.005).

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