Note

A new tris(ferrocenylamine) ditertiary phosphine: Synthesis and co-ordination studies

Mark R.J. Elsegood, Andrew J. Lake, Roger J. Mortimer, Martin B. Smith*, George W. Weaver

Department of Chemistry, Loughborough University, Loughborough, Leics LE11 3TU, UK

ABSTRACT

The new tris(ferrocenylamine) ditertiary phosphine 1,1'-{FcCH$_2$N(CH$_2$PPh$_2$)CH$_2$(η^5-C$_5$H$_4$)}$_2$Fe [Fc = (η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$)] has been prepared along with two coordination complexes. All compounds have been characterised by a combination of spectroscopic and analytical methods. The single crystal X-ray structure of the pentametallic Ru$_2$Fe$_3$ complex **5** has been determined.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The ferrocenyl (Fc) group continues to play an important role in the design of new ligands especially those containing phosphorus [1–3]. One plausible reason for the success of the Fc group can possibly be traced to the ease by which this substituent can be placed within a ligand structure i.e. terminal (P–Fc) or as a backbone connector (P–Fc–P). Consequently the incorporation of a Fc moiety has allowed the preparation of various functionalised ferrocenyl phosphine [4,5], diphosphine [6,7] and polyphosphine [8,9] or macrocyclic [10] ligands to be realised. Considerable interest in ferrocenyl phosphines continues as a result of their interesting catalytic [11–14] and cytotoxic [15,16] properties. Furthermore ferrocenyl based compounds also 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 [17–20]. We report here the synthesis of a new ditertiary phosphine bearing three ferrocenyl groups and some coordination studies towards Ru^{II} and Au^{I} metal centres. The electrochemical properties of selected compounds are also reported along with a single crystal X-ray structure determination of a new pentametallic Ru$_2$Fe$_3$ complex.

2. Experimental

2.1. Materials

Standard Schlenk techniques were used for the synthesis of **3** whilst all other reactions were carried out in air using previously distilled solvents unless otherwise stated. Diphenylphosphinomethanol has been reported elsewhere [21] and the metal precursors {RuCl(μ-Cl)(η^6-p-cym)}$_2$ (p-cym = p-cymene) [22] and AuCl(tht) (tht = tetrahydrothiophene) [23] were prepared according to known procedures. The ferrocenyl precursors 1,1'-(C$_5$H$_4$CHO)$_2$Fe [24a] and FcCH$_2$NH$_2$ [24b] were prepared following previously reported methods. 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 4000–400 cm^{-1} on a Perkin-Elmer System 2000 Fourier-transform spectrometer. ^{1}H 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{^{1}H} NMR spectra were recorded on a Bruker DPX-400 FT spectrometer with chemical shifts (δ) in ppm to high frequency of 85% H$_3$PO$_4$. All NMR spectra were measured in CDCl$_3$. Elemental analyses (Perkin-Elmer 2400 CHN or Exeter Analytical, Inc. CE-440 Elemental Analyzers) were performed by the Loughborough University Analytical Service within the

* Corresponding author. Tel.: +44 1509 222553; fax: +44 1509 223925.
E-mail address: m.b.smith@lboro.ac.uk (M.B. Smith).

Department of Chemistry. Mass spectra were recorded within the Department of Chemistry at Loughborough University and by the EPSRC National Mass Spectrometry Service at Swansea University.

2.3. Syntheses

2.3.1. 1,1′-{FcCH$_2$NC(H)(η^5-C$_5$H$_4$)}$_2$Fc (1)

The imine 1,1′-{FcCH$_2$NC(H)}$_2$Fc **1** was synthesised following minor modification of a literature method [25]. To a refluxing solution of 1,1′-(C$_5$H$_4$CHO)$_2$Fe (0.205 g, 0.847 mmol) in methanol (40 mL) was added dropwise a solution of FcCH$_2$NH$_2$ (0.364 g, 1.69 mmol) in methanol (20 mL). The red solution was refluxed for 4 h, cooled to room temperature and the solvent evaporated under reduced pressure. Yield: Quantitative. Selected data for **1**: ^{1}H NMR (CDCl$_3$): δ 7.93 (s, 2H, CHN), 4.52 (s, 4H, CH$_2$C$_5$H$_4$), 4.35−4.09 (m, 26H, C$_5$H$_4$ and C$_5$H$_5$). FT-IR (KBr): $\nu_{C=N}$ 1636 cm^{-1}. MS (FAB$^+$): m/z 636 [M]$^+$. Anal. Calc. for C$_{34}$H$_{32}$N$_2$Fe$_3$·0.5H$_2$O requires: C, 63.29; H, 5.16; N, 4.34. Found: C, 63.05; H, 5.21; N, 4.23%.

2.3.2. 1,1′-{FcCH$_2$N(H)CH$_2$(η^5-C$_5$H$_4$)}$_2$Fe (2)

The secondary amine 1,1′-{FcCH$_2$N(H)CH$_2$}$_2$Fe **2** was prepared following minor adaptation of a known procedure [25]. NaBH$_4$ (0.183 g, 4.74 mmol) was added to a stirred solution of **1** (0.498 g, 0.783 mmol) in CH$_2$Cl$_2$:EtOH (60 mL, 2:1). The resulting suspension was refluxed for 4 h under a N$_2$ atmosphere and cooled to room temperature to afford an orange solution. Concentrated HCl was added dropwise until effervescence subsided, the solvent volume reduced in vacuo and aqueous NaOH solution (2.5 g, 60 mL) added. The resulting suspension was stirred briefly and the organic phase extracted into CHCl$_3$ (60 mL), dried over anhydrous MgSO$_4$ and the solvent evaporated to dryness under reduced pressure. Yield: Quantitative. Selected data for **2**: ^{1}H NMR (CDCl$_3$): δ 4.12 (s, 8H, C$_5$H$_4$), 4.04 (s, 10H, C$_5$H$_5$), 3.99 (s, 8H, C$_5$H$_4$), 3.45 (bs, 8H, CH$_2$C$_5$H$_4$). FT-IR (KBr): ν_{NH} 3091 cm^{-1}. MS (FAB$^+$): m/z 640 [M]$^+$. Anal. Calc. for C$_{34}$H$_{36}$N$_2$Fe$_3$·1.5H$_2$O requires: C, 61.20; H, 5.89; N, 4.20. Found: C, 61.14; H, 5.88; N, 3.90%.

2.3.3. 1,1′-{FcCH$_2$N(CH$_2$PPh$_2$)CH$_2$(η^5-C$_5$H$_4$)}$_2$Fe (3)

Under a N$_2$ atmosphere, a solution of **2** (0.309 g, 0.483 mmol) and Ph$_2$PCH$_2$OH (0.223 g, 0.959 mmol) in C$_7$H$_8$:MeOH (20 mL, 2:1) was stirred for 44 h at r.t. The solvent was removed under reduced pressure. Crude yield: Quantitative. Selected data for **3**: ^{31}P{^{1}H} NMR (CDCl$_3$): δ −27.8 (s) ppm. ^{1}H NMR (CDCl$_3$): δ 7.42−7.07 (m, 20H, arom. H), 4.08 (s, 4H, C$_5$H$_4$), 4.04 (s, 4H, C$_5$H$_4$), 4.00 (s, 10H, C$_5$H$_5$), 3.98 (s, 8H, C$_5$H$_4$), 3.55 (s, 4H, CH$_2$C$_5$H$_4$), 3.51 (s, 4H, CH$_2$C$_5$H$_4$), 3.02 (d, 4H, $^2J_{PH}$ 3.6 Hz, CH$_2$P). Attempts to obtain an analytically pure sample of **3** were unsuccessful.

2.3.4. 1,1′-{FcCH$_2$N(CH$_2$PPh$_2$AuCl)CH$_2$(η^5-C$_5$H$_4$)}$_2$Fc (4)

A colourless solution of AuCl(tht) (0.118 g, 0.368 mmol) in CH$_2$Cl$_2$ (5 mL) was added to a stirred solution of **3** (0.222 g, 0.186 mmol) in CH$_2$Cl$_2$ (5 mL). The resulting solution was stirred, in the dark, for 1 h and concentrated under reduced pressure to *ca.* 2 mL. Hexane (25 mL) was added and the resulting yellow suspension stirred for a further 0.5 h. The precipitate was filtered and dried under reduced pressure. Yield: 0.239 g, 87%. Selected data for **4**: ^{31}P{^{1}H} NMR (CDCl$_3$): δ 17.4 (s) ppm. ^{1}H NMR (CDCl$_3$): δ 7.71−7.25 (m, 20H, arom. H), 4.02 (m, 26H, C$_5$H$_4$ and C$_5$H$_5$), 3.81 (s, 4H, CH$_2$), 3.56 (s, 4H, CH$_2$), 3.44 (s, 4H, CH$_2$). MS (FAB$^+$): m/z 1233 [M−AuCl−Cl]$^+$. Anal. Calc. for C$_{60}$H$_{58}$N$_2$Fe$_3$P$_2$Au$_2$Cl$_2$·0.75C$_6$H$_{14}$ requires: C, 49.47; H, 4.41; N, 1.79. Found: C, 49.40; H, 4.43; N, 1.79%.

2.3.5. 1,1′-{FcCH$_2$N{CH$_2$PPh$_2$RuCl$_2$(η^6-p-cym)}CH$_2$(η^5-C$_5$H$_4$)}$_2$Fc (5)

{RuCl(μ-Cl)(η^6-p-cym)}$_2$ (0.083 g, 0.136 mmol), **3** (0.162 g, 0.136 mmol) and CH$_2$Cl$_2$ (10 mL). Yield: 0.136 g, 61%. Selected data

for **5**: ^{31}P{^{1}H} NMR (CDCl$_3$): 26.1 (s) ppm. ^{1}H NMR (CDCl$_3$): δ 7.93−7.36 (m, 20H, arom. H), 5.13 (d, 4H, $^3J_{HH}$ 5.2 Hz, CH), 5.06 (d, 4H, $^3J_{HH}$ 5.2 Hz, CH), 3.92 (s, 4H, C$_5$H$_4$), 3.82 (s, 4H, C$_5$H$_4$), 3.77 (s, 14H, C$_5$H$_5$ and C$_5$H$_4$), 3.62 (s, 4H, C$_5$H$_4$), 3.42 (s, 4H, CH$_2$P), 2.59 (s, 4H, CH$_2$C$_5$H$_4$), 2.49 (s, 4H, CH$_2$C$_5$H$_4$), 2.35 (sept, 2H, $^3J_{HH}$ 6.8 Hz, CH), 1.71 (s, 6H, CH$_3$), 0.85 (d, 12H, $^3J_{HH}$ 6.8 Hz, CH$_3$). MS (FAB$^+$): m/z 1651 [M]$^+$. Anal. Calc. for C$_{80}$H$_{86}$N$_2$Fe$_3$P$_2$Ru$_2$Cl$_4$ requires: C, 58.20; H, 5.25; N, 1.70. Found: C, 57.80; H, 5.26; N, 1.78%.

2.4. X-ray crystallography

Suitable crystals of **5**·4CH$_2$Cl$_2$ were obtained by slow diffusion of Et$_2$O into a CH$_2$Cl$_2$ solution of **5**. Details of the data collection parameters and crystal data for **5**·4CH$_2$Cl$_2$ are given in Table 1. Measurements for **5**·4CH$_2$Cl$_2$ were made on a Bruker Apex 2 CCD diffractometer using graphite monochromated radiation from a sealed tube Mo-K$_\alpha$ source. Narrow frame ω-scans were employed and intensities were corrected semi-empirically for absorption, based on symmetry-equivalent and repeated reflections. The structure of **5**·4CH$_2$Cl$_2$ was solved by direct methods 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_{eq} of the carrier atom (1.5U_{eq} for methyl hydrogen). One badly disordered molecule of CH$_2$Cl$_2$ per complex was modelled by the Platon Squeeze procedure [26]. The cyclopentadienyl ring containing C(43)−C(47) was found to be disordered over two sets of positions; major occupancy = 54.29(2)%, for which the geometry and aniso-tropic displacement parameters of both disorder components were restrained to be similar. Programs used were Bruker AXS APEX2 [27] for diffractometer control and SAINT for frame integration [28], Bruker SHELXTL [29] for structure solution, refinement, and molecular graphics and local programs.

2.5. Electrochemistry

Cyclic voltammetric measurements for **1**−**4** 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

Table 1
Crystallographic data for **5**·4CH$_2$Cl$_2$.

Empirical formula	C$_{84}$H$_{94}$Cl$_{12}$Fe$_3$N$_2$P$_2$Ru$_2$
Formula weight	1988.64
Crystal system	Triclinic
Space group	P $\bar{1}$
a (Å)	11.6191(7)
b (Å)	19.8758(12)
c (Å)	20.5317(13)
α (°)	101.5303(11)
β (°)	104.1117(11)
γ (°)	105.8676(11)
Volume (Å^3)	4238.8(5)
Z	2
λ	0.71073
T (K)	150(2)
D_{calc} (mg/m^3)	1.558
Absorption coefficient (mm^{-1})	1.310
Crystal habit and colour	Plate; orange
Crystal size (mm^3)	0.25 × 0.21 × 0.07
θ Range (°)	1.11–26.00
Reflections collected	37,260
Independent reflections [R_{int}]	16,638 [0.0518]
Completeness (%)	99.8
Number of parameters	971
Final R[a], Rw[b]	0.067, 0.208

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

[b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$.

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 $[NBu_4][BF_4]$ (0.1 M) as the supporting electrolyte. Ferrocene was used as an external standard.

3. Results and discussion

3.1. Ligand synthesis

Ferrocenyl derived phosphines have been accessed through a number of established methods [1–3]. In our work we have found phosphorus based Mannich condensation reactions are extremely versatile procedures for preparing new phosphine ligands [18,30]. The new trimetallophosphine **3** was prepared by a non-optimised double condensation of the parent secondary amine, 1,1'-{FcCH$_2$N (H)CH$_2$(η^5-C$_5$H$_4$)}$_2$Fe **2**, with two equiv. of Ph$_2$PCH$_2$OH. To the best of our knowledge precursors **1** and **2** have not previously been reported (Experimental section for characterising details). The trimetallophosphine **3** was obtained as a viscous oil following complete removal of the solvent and the ^{31}P{^{1}H} NMR spectrum (in CDCl$_3$) of this oil exhibited a major phosphorus resonance at δ(P) −27.8 ppm (ca. 85% by integration) consistent with previous literature values [18]. Unreacted Ph$_2$PCH$_2$OH and Ph$_2$PH were the only other minor P^{III} species present. The ^{1}H NMR spectrum (in CDCl$_3$) of impure **3** confirmed the characteristic doublet [18] at δ(H) 3.02 ppm ($^2J_{PH}$ 3.6 Hz) for the CH$_2$P methylene protons. Further evidence for the preparation of **3** came from the significantly reduced intensity of the ν_{NH} absorption band in the FT-IR spectrum compared to **2**. The formation of **3** was further supported by subsequent coordination chemistry using this isolated oil (*vide infra*) as shown in scheme 1.

3.2. Coordination studies

The coordination chemistry of the new trimetalloligand **3** was briefly explored by reaction with two readily available transition metal starting materials. Hence treatment of **3** with AuCl(tht) (2 equiv.) or {RuCl(μ-Cl)(η^6-*p*-cym)}$_2$ (1 equiv.) in CH$_2$Cl$_2$ at ambient temperature gave the pentametallic complexes **4** and **5** in moderate to excellent yield (61 and 87% respectively). The ^{31}P{^{1}H} NMR spectrum (in CDCl$_3$) of **4** displayed a new low field resonance at δ(P) 17.4 ppm. In contrast, the ^{31}P{^{1}H} NMR spectrum (in CDCl$_3$) of **5** contained three distinct singlet resonances at δ(P) 26.1, 21.0 and 16.1 ppm. The major singlet at δ(P) 26.1 ppm was assigned to **5** by comparison of this data with a related ruthenium *p*-cym complex [18]. The minor δ(P) signals at 21.0 ppm and 16.1 ppm were confidently assigned to RuCl$_2$(η^6-*p*-cym)(Ph$_2$PH) and RuCl$_2$(η^6-*p*-cym) (Ph$_2$PCH$_2$OH) respectively [31]. For **4** and **5** the ^{1}H NMR (in CDCl$_3$) spectra displayed the anticipated resonances for both complexes. Further support for the preparation of the new pentametallic complexes **4** and **5** comes from positive ion FAB mass spectroscopy which displayed fragments at *m/z* 1233 [M−AuCl−Cl]$^+$ (**4**) and 1651 [M]$^+$ (**5**). The molecular structure of **5**·4CH$_2$Cl$_2$ has been determined by single crystal X-ray diffraction and confirms the bridging nature of the trimetalloligand **3** (Section 3.3).

3.3. Single crystal X-ray study of **5**·4CH$_2$Cl$_2$

The single crystal X-ray structure of **5**·4CH$_2$Cl$_2$ (Fig. 1) has been determined and selected bond lengths and angles are given in Table 2. The trimetalloligand was shown to bridge two {RuCl$_2$(*p*-cym)} fragments by coordination to both P(III) atoms. In each case the ruthenium centre was shown to adopt a characteristic piano-stool geometry with normal Ru−Cl, Ru−P and Ru−(*p*-cym$_{cent}$) distances [18]. The phosphorus atoms were found to adopt a distorted

ML$_n$ = AuCl   **4**
ML$_n$ = RuCl$_2$(η^6–*p*–cym)   **5**
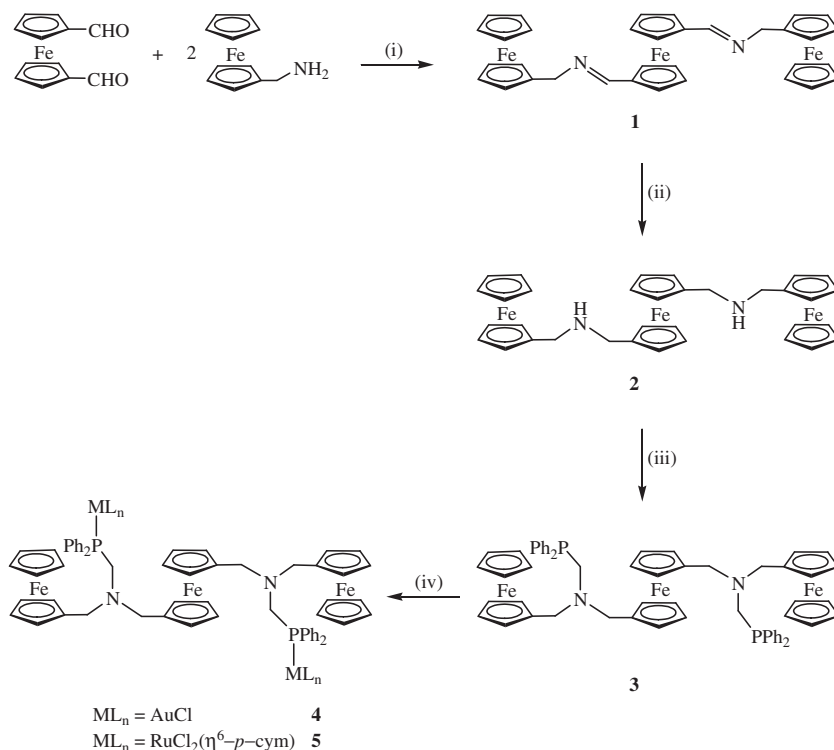
Scheme 1. Synthesis of compounds **1–5**. (i) MeOH, (ii) NaBH$_4$, (iii) Ph$_2$PCH$_2$OH, (iv) AuCl(tht), or {RuCl(μ-Cl)(η^6-*p*-cym)}$_2$.
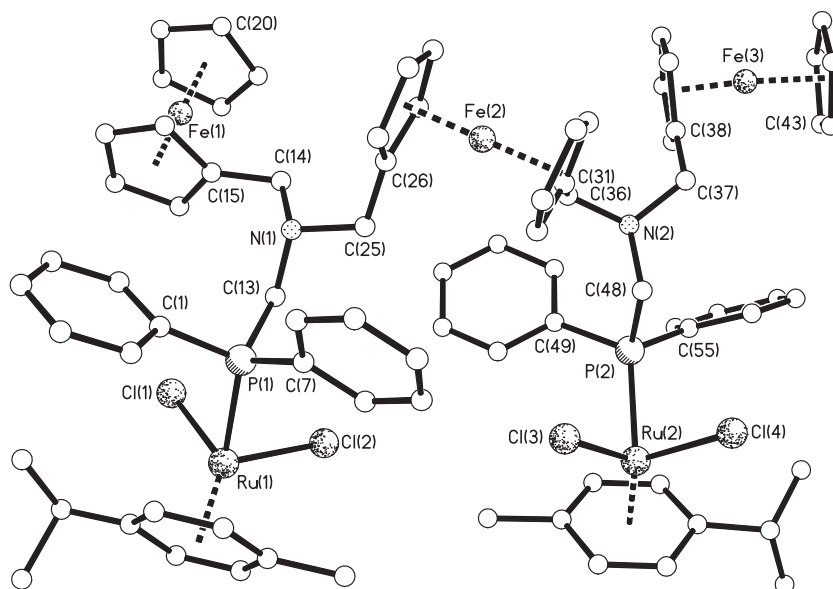
Fig. 1. X-ray structure of **5**·4CH$_2$Cl$_2$. All hydrogen atoms and solvent molecules of crystallisation have been removed for clarity.

pyramidal geometry, as indicated by the relevant C–P–Ru angles [C–P–Ru ranged between 111.50(19)–116.7(2)°], whilst the nitrogen atoms adopted a distorted trigonal pyramidal arrangement [$\Sigma = 328°$ for N(1) and 343° for N(2)]. The geometry around each ferrocenyl moiety is regular showing approximately equal Fe···Cp$_{cent}$ bond lengths [range 1.6212(31)–1.652(15) Å]. Furthermore the cyclopentadienyl rings of ferrocene are eclipsed and essentially coplanar [torsional twist angles about the Cp$_{cent}$···Fe···Cp$_{cent}$ are 7.3° at Fe(1), 10.5° at Fe(2) and 13.8° at

Fe(3)]. The C(26)···Cp(C)$_{cent}$···Cp(D)$_{cent}$···C(31) torsion angle is 60.45° suggesting a synclinal eclipsed conformation of the {FcCH$_2$N {CH$_2$PPh$_2$RuCl$_2$(η^6-p-cym)}CH$_2$– groups [3]. The internuclear distances between the Fe^{II} centres are 7.721, 7.488 and 11.968 Å for Fe(1)···Fe(2), Fe(2)···Fe(3) and Fe(1)···Fe(3) respectively while the Ru(1)···Ru(2) separation is 8.402 Å.

3.4. Electrochemical properties

The electrochemical properties of **1**–**4** have been investigated by cyclic voltammetry, and their oxidation (E_{pa}) and reduction (E_{pc}) potentials summarised in Table 3. For the imine **1**, the cyclic voltammogram displayed a reversible ferrocene/ferrocenium redox (Fc/Fc$^+$) couple similar to that of ferrocene, at $E_{1/2}$ −0.042 V, in addition to a further ferrocene/ferrocenium oxidation peak (E_{pa}) at +0.279 V (Fig. 2).

The reversible ferrocene/ferrocenium redox (Fc/Fc$^+$) couple at $E_{1/2}$ −0.042 V was found to be similar to that of {FcCH$_2$N(CH$_2$PPh$_2$) CH$_2$}$_2$ [18] suggesting that the terminal ferrocenyl groups (Fc$_t$) in **1** also undergo simultaneous oxidation and reduction. The second oxidation potential at E_{pa} +0.279 V was assigned to the bridging ferrocenyl moiety (Fc$_b$) within the imine. Closer inspection of the voltammogram revealed a slight shoulder at 0.096 V (Fig. 2 highlighted by *) which was cautiously assigned to the reversible reduction peak (E_{pc}) of the bridging ferrocenyl group, to give a ferrocene/ferrocenium redox (Fc/Fc$^+$) couple for Fc$_b$ at $E_{1/2}$ +0.188 V. The assignment of these two distinct ferrocenyl environments, within the cyclic voltammogram of **1**, is supported by the characteristic distribution (ca. 2:1 by integration) of charge

Table 2
Selected bond lengths and angles for **5**·4CH$_2$Cl$_2$.

Ru(1)–Cl(1)	2.4107(18)	P(1)–Ru(1)–Cl(1)	83.57(6)
Ru(1)–Cl(2)	2.4079(18)	P(1)–Ru(1)–Cl(2)	89.28(6)
Ru(2)–Cl(3)	2.4107(16)	Cl(1)–Ru(1)–Cl(2)	87.83(6)
Ru(2)–Cl(4)	2.4160(17)	P(2)–Ru(2)–Cl(3)	86.96(6)
Ru(1)–P(1)	2.3597(16)	P(2)–Ru(2)–Cl(4)	85.34(6)
P(1)–C(1)	1.818(6)	Cl(3)–Ru(2)–Cl(4)	87.21(6)
P(1)–C(7)	1.821(6)	Ru(1)–P(1)–C(1)	111.50(19)
P(1)–C(13)	1.838(6)	Ru(1)–P(1)–C(7)	115.5(2)
Ru(2)–P(2)	2.3403(16)	Ru(1)–P(1)–C(13)	112.04(19)
P(2)–C(48)	1.854(6)	P(1)–C(13)–N(1)	117.6(4)
P(2)–C(49)	1.833(6)	C(13)–N(1)–C(14)	109.8(4)
P(2)–C(55)	1.823(6)	C(13)–N(1)–C(25)	110.1(4)
N(1)–C(13)	1.467(7)	C(14)–N(1)–C(25)	108.5(4)
N(1)–C(14)	1.489(7)	C(37)–N(2)–C(48)	115.8(5)
N(1)–C(25)	1.500(7)	C(36)–N(2)–C(37)	114.8(5)
N(2)–C(36)	1.469(7)	C(36)–N(2)–C(48)	112.5(5)
N(2)–C(37)	1.458(8)	P(2)–C(48)–N(2)	109.9(4)
N(2)–C(48)	1.463(7)	Ru(2)–P(2)–C(48)	116.42(19)
Ru(1)···cym$_{cent}$	1.701(3)	Ru(2)–P(2)–C(49)	116.7(2)
Ru(2)···cym$_{cent}$	1.703(3)	Ru(2)–P(2)–C(55)	112.5(2)
Fe(1)···Cp(A)$_{cent}$[a]	1.621(3)	C(15)–Cp(A)$_{cent}$–Cp(B)$_{cent}$–C(21)[a]	7.3
Fe(1)···Cp(B)$_{cent}$[a]	1.643(3)	C(26)–Cp(C)$_{cent}$–Cp(D)$_{cent}$–C(32)[a]	10.5
Fe(2)···Cp(C)$_{cent}$[a]	1.645(3)	C(38)–Cp(E)$_{cent}$–Cp(F)$_{cent}$–C(44)[a,b]	13.8
Fe(2)···Cp(D)$_{cent}$[a]	1.649(3)	C(38)–Cp(E)$_{cent}$–Cp(G)$_{cent}$–C(44)[a,c]	−13.9
Fe(3)···Cp(E)$_{cent}$[a]	1.640(2)		
Fe(3)···Cp(F)$_{cent}$[a,b]	1.652(15)		
Fe(3)···Cp(G)$_{cent}$[a,c]	1.668(15)		

[a] Cp(A)$_{cent}$ = C(15)–C(19), Cp(B)$_{cent}$ = C(20)–C(24), Cp(C)$_{cent}$ = C(26)–C(30), Cp (D)$_{cent}$ = C(31)–C(35), Cp(E)$_{cent}$ = C(38)–C(42), Cp(F)$_{cent}$ = C(43)–C(47), Cp(G)$_{cent}$ = C(43X)–C(47X).
[b] Major disorder component.
[c] Minor disorder component.

Table 3
Electrochemical data for compounds **1**–**4**.[a]

Compound	$E_{pa}(V)$[b], Fe$^{II/III}$	$E_{pc}(V)$[b], Fe$^{II/III}$
1	+0.006, +0.279	−0.090
2	+0.016, +0.154	+0.022
3	+0.218	+0.064
4	+0.105	−0.034

[a] All experiments were performed in a 0.1 M [NBu$_4$][BF$_4$]/dry CH$_2$Cl$_2$ solution using a standard electrochemical cell at a scan rate of 50 mV/s.
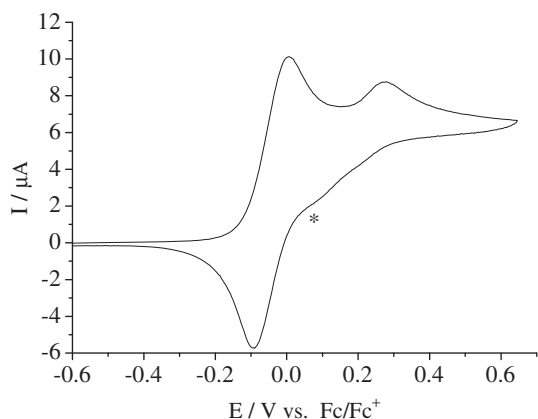[b] E_{pc} and E_{pa} reported relative to the ferrocene/ferrocenium couple.

Fig. 2. Cyclic voltammogram of **1** in dry CH_2Cl_2, 0.1 M [NBu$_4$][BF$_4$] at a scan rate of 50 mV s^{-1}. Suggested reduction potential (E_{pc}) of bridging ferrocenyl moiety (*). Electrical potentials quoted relative to the ferrocene/ferrocenium redox (Fc/Fc$^+$) couple.

between the two redox waves for the terminal (Fc$_t$) and bridging (Fc$_b$) ferrocenyl groups.

In contrast the voltammogram of **3**, along with the parent amine **2**, showed less resolved ferrocene/ferrocenium redox (Fc/Fc$^+$) couples compared to **1**, suggesting that as the bonds between neighbouring ferrocenyl groups become more saturated, the more electrochemically similar the distinct ferrocenyl environments become. This increasing similarity between the various ferrocene/ferrocenium environments was mirrored in the voltammogram of the pentametallic complex **4** which contained a single broad ferrocene/ferrocenium redox couple at $E_{1/2}$ 0.036 V, indicating that the three redox couples are only marginally different. The $E_{1/2}$ of **4** was also found to be similar to the gold(I) complex {FcCH$_2$N(CH$_2$PPh$_2$AuCl)CH$_2$}$_2$ [$E_{1/2}$ +0.012 V, $\Delta E_{1/2}$ 0.024 V] [18] reported by us, suggesting that the electrochemical properties of the terminal ferrocenyl groups are not significantly altered by variation of the "linker" between the electrochemically active termini.

4. Conclusions

In summary, we have shown that a new ditertiary phosphine containing three ferrocenyl groups can be prepared and shown to bridge either two Ru^{II} or Au^I metal centres. The electrochemical properties of selected compounds have been investigated along with the molecular structure of a new Ru$_2$Fe$_3$ complex.

Acknowledgements

Appendix A. Supplementary material

A complete set of X-ray crystallographic structural data for compound **5** (CCDC no. 751099) is available at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.ac.uk) on request, quoting the deposition number.

Appendix B. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.04.012.

References

[1] (a) J.-C. Hierso, R. Smaliy, R. Amardeil, P. Meunier, Chem. Soc. Rev. 36 (2007) 1754;
(b) J.-C. Hierso, M. Beaupérin, P. Meunier, Eur. J. Inorg. Chem. (2007) 3767.
[2] R.C.J. Atkinson, V.C. Gibson, N.J. Long, Chem. Soc. Rev. 33 (2004) 313.
[3] G. Bandoli, A. Dolmella, Coord. Chem. Rev. 209 (2000) 161.
[4] J. Kühnert, I. Císařová, M. Lamač, P. Štěpnička, Dalton Trans. (2008) 2454.
[5] M. Lamač, J. Cvačka, P. Štěpnička, J. Organomet. Chem. 693 (2008) 3430.
[6] A.P. Shaw, J.R. Norton, D. Buccella, L.A. Sites, S.S. Kleinbach, D.A. Jarem, K.M. Bocage, C. Nataro, Organometallics 28 (2009) 3804.
[7] E.J. Velazco, A.J.M. Caffyn, X.F. Le Goff, L. Ricard, Organometallics 27 (2008) 2402.
[8] A. Pascariu, S. Iliescu, A. Popa, G. Ilia, J. Organomet. Chem. 694 (2009) 3982.
[9] A. Jahel, N.V. Vologdin, N. Pirio, H. Cattey, P. Richard, P. Meunier, J.-C. Hierso, Dalton Trans. (2008) 4206.
[10] T. Mizuta, T. Aotani, Y. Imamura, K. Kubo, K. Miyoshi, Organometallics 27 (2008) 2457.
[11] J. Tauchman, I. Císařová, P. Štěpnička, Organometallics 28 (2009) 3288.
[12] G.A. Grasa, T.J. Colacot, Org. Lett. 9 (2007) 5489.
[13] B. Lipshutz, B.R. Taft, Org. Lett. 10 (2008) 1329.
[14] D.-Y. Zou, Z.-C. Duan, X.-P. Hu, Z. Zheng, Tetrahedron: Asymmetry 20 (2009) 235.
[15] M. Auzias, B. Therrien, G. Suss-Fink, P. Štěpnička, W.H. Ang, P.J. Dyson, Inorg. Chem. 47 (2008) 578.
[16] O. Payen, S. Top, A. Vessières, E. Brulé, M.-A. Plamont, M.J. McGlinchey, H. Müller-Bunz, G. Jaouen, J. Med. Chem. 51 (2008) 1791.
[17] M. Arroyo, P.R. Birkin, P.A. Gale, S.E. García-Garrido, M.E. Light, New J. Chem. 32 (2008) 1221.
[18] M.R.J. Elsegood, A.J. Lake, R.J. Mortimer, M.B. Smith, G.W. Weaver, J. Organomet. Chem. 693 (2008) 2317.
[19] M. Lohan, P. Ecorchard, T. Rüffer, F. Justaud, C. Lapinte, H. Lang, Organometallics 28 (2009) 1878.
[20] A. Jakob, P. Ecorchard, M. Linseis, R.F. Winter, H. Lang, J. Organomet. Chem. 694 (2009) 655.
[21] H. Hellmann, J. Bader, H. Birkner, O. Schumacher, J. Liebigs Ann. Chem. 659 (1962) 49.
[22] M.A. Bennett, A.K. Smith, J. Chem. Soc. Dalton Trans. (1974) 233.
[23] R. Uson, A. Laguna, M. Laguna, Inorg. Synth. 26 (1989) 85.
[24] (a) G.G.A. Balavoine, G. Doisneau, T. Fillebeen-Khan, J. Organomet. Chem. 412 (1991) 381;
(b) P.D. Beer, D.K. Smith, J. Chem. Soc. Dalton Trans. (1998) 417.
[25] (a) G. Zhang, G. Yang, L. Yang, Q. Chen, J.-S. Ma, Eur. J. Inorg. Chem. (2005) 1919;
(b) A. Benito, J. Cano, R. Martínez-Máñez, J. Soto, J. Payá, F. Lloret, M. Julve, J. Faus, M.D. Marcos, Inorg. Chem. 32 (1993) 1197.
[26] A.L. Spek, Acta Crystallogr. Sect. A 46 (1990) C34.
[27] APEX 2 User Manual. Bruker AXS Inc., Madison, WI, 2006.
[28] SAINT Software for CCD Diffractometers. Bruker AXS Inc., Madison, WI, 2006.
[29] (a) G.M. Sheldrick, SHELXTL User Manual, Version 6.10. Bruker AXS Inc., Madison, WI, 2000;
(b) G.M. Sheldrick, Acta Crystallogr. Sect. A 64 (2008) 112.
[30] M.R.J. Elsegood, A.J. Lake, M.B. Smith, Dalton Trans. (2009) 30.
[31] S.E. Dann, S.E. Durran, M.R.J. Elsegood, M.B. Smith, P.M. Staniland, S. Talib, S.H. Dale, J. Organomet. Chem. 691 (2006) 4829.