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Synthesis, crystal structure and comparative electrochemistry of metallocenyldiphenylphosphines of ruthenocene, osmocene, ferrocene and cobaltocenium hexafluorophosphate



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ABSTRACT

The metallocenyldiphenylphosphines $[M(C_5H_5)(C_5H_4PPh_2)]$ with M = Fe(II) (ferrocenyl = Fc), 1, Ru(II) (ruthenocenyl = Rc), **2**, Os(II) (osmocenyl = Oc), **3**, and $Co(III)^+PF_6^-$ (cobaltocenium hexafluorophosphate = $[Cc][PF_6]$, **4**, were synthesized and the crystal structure of RcPPh₂, **2**, (Z = 4, monoclinic, space group $P2_1/c$) was determined. The differences in reactivity of each metallocenyl derivative were such that 1 could be obtained from a Friedel Crafts reaction between ferrocene and PPh₂Cl in the presence of AlCl₃ as catalyst. Both the ruthenocene and osmocene derivatives 2 and 3 were obtained by reacting the monolithiated metallocene precursor with PPh₂Cl. However, monolithiation of ruthenocene had to be achieved via a stoichiometric amount of ^tBuLi. For osmocene, monolithiation was achieved by a 20% excess of ⁿBuLi. This was evidenced by the failure to isolate any bisphosphine, Oc(PPh₂)₂, during workup. Complex **4** could not be obtained via phosphination of free cobaltocenium hexafluorophosphate. Phosphine derivatisation of free cyclopentadiene prior to complexation with Co^{III} was required to form [CcPPh2][PF6], 4. The electrochemistry of all phosphines was studied by voltammetric techniques in $CH_2Cl_2/0.1$ mol dm⁻³ [N(ⁿBu)₄][B(C₆F₅)₄]. A reversible one-electron transfer process for the ferrocenyl group of 1 was observed at 0.078 V vs. FcH/FcH⁺. The osmocenyl and ruthenocenyl derivatives exhibited irreversible metallocenyl oxidations at 0.355 and 0.476 V respectively. The cobaltocenium complex, 4, exhibited two reversible one-electron transfer reductions to liberate first a neutral Co^{II} cobaltocene species at -1.062 V and then an anionic Co^{II} cobaltocene species at -2.122 V. A single electrochemical irreversible, one-electron oxidation at the phosphorus centre which forms a quicklydecomposing phosphorus radical cation, Mc⁺Ph₂P⁺, was also observed at $E_{pa} > 0.754$ V. The newlyformed Mc⁺Ph₂P⁺⁺ species or its chemical decomposition products can be oxidized at $E_{\rm pa} > 1.090$ V vs. FcH/FcH⁺.

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1. Introduction

Incorporating metallocenes as part of a phosphine ligand creates very useful ligands for catalytic processes [1]. The value of phosphines as ligand components stem from their unique and very specific geometries, as well as their electronic properties [2]. The ferrocenyl (Fc), ruthenocenyl (Rc) and osmocenyl (Oc) groups are all strongly electron donating substituents that increase the electron density of most of the species that it is bound to substantially [3]. This property leads to a substantial increase in the rate of oxidative addition of methyl iodide to ferrocene-containing β -diketonato complexes [Rh(FcCOCHCOR)(CO)(PPh₃)] [4], but to a decrease in the rate of β -diketonato substitution with phenanthroline in complexes of the type [Rh(FcCOCHCOR)(cod)] [5] where R = Fc, Ph, CH₃ or CF₃. Ferrocenes are frequently the substance of choice to employ in energy [6] and electron-transfer processes because of their reversible one-electron redox behaviour [7], ease of chemical modification [8] and high thermal stability [9]. The cytotoxic properties of ferrocene derivatives [10] are also related to the redox potentials of the ferrocenyl group [11].

The electrochemistry of ruthenocene differs from that of ferrocene in that oxidation of the ruthenocenyl group to the unstable 17 electron monomeric ruthenocenium species can only be achieved in solvents that have no propensity towards solvation, such as CH_2Cl_2 , while simultaneously using electrolyte systems such as $[N(^nBu)_4][B\{C_6H_3(CF_3)_2\}_4]$ or $[N(^nBu)_4][B(C_6F_5)_4]$ [12]. These electrolytes do not form ion pares of the type Rc⁺...⁻ (electrolyte anion). The ruthenocenium cation, Rc⁺, spontaneously dimerizes

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into two separate dimers, one of which dominates at room temperature. The other dominates at low $(-40 \ ^{\circ}C)$ temperature [13]. Although the organic chemistry of ruthenocene parallels that of ferrocene, this metallocene does not undergo chemical modification, *e.g.* acetylation reactions, as readily as ferrocene [14].

The chemical modification of cobaltocene is difficult to achieve and functionalization usually takes place on free cyclopentadienyl rings prior to coordination with cobalt [15]. Cobaltocene itself containing a Co(II) nucleus is very air sensitive but the cobaltocenium cation bearing a Co(III) centre is stable in air [16]. Geiger [17] reported two reversible electrochemical one-electron reductions for the cobaltocenium cation, the first involving the Co^{II/III} couple at -0.94 V vs. FcH/FcH⁺, and the second a Co^{I/II} couple at -1.88 V. Being cationic, the cobaltocenium group is expected to be very electron-withdrawing.

The chemical oxidation of osmocene [18] parallels the above described electrochemical oxidation of ruthenocene [13]. Taube isolated both dimers of oxidized osmocene and reported their crystal structures [18]. Osmocene must also form these dimers electrochemically, but on CV time-scale they were not yet identified.

In contrast to the wealth of knowledge available on metallocenylbisphosphines [1,2,19,20], only ferrocene- and ruthenocenecontaining monophosphines are known [21]. The mono, di and tri ferrocenylated monophosphines FcPPh₂, Fc₂PPh and Fc₃P have been synthesized under Friedel Crafts conditions in the presence of AlCl₃ via a stepwise process [22]. They are all readily air-oxidized in the presence of aluminium trichloride. However, similar to triphenylphosphine, FcPPh₂ and Fc₂PPh do show appreciable stability towards air oxidation when isolated and stored in the solid state [23]. The σ -donor ability of these ligands was found to increase with the increasing number of ferrocenyl groups. Electrochemically, FcPPh₂ [24,25] shows two irreversible oxidation peaks at approximately $E_{pa} = 0.48$ V (for ferrocenyl) and 1.5 V (for phosphorus) vs SCE, as well as a reduction peak at approximately $E_{\rm pc} = 0.5$ V. The first (ferrocenyl) oxidation process becomes reversible when the positive scan direction is reversed at 0.8 V, before the phosphorus oxidation process at $E_{pa} = 1.5$ V can take place. Under such conditions the reduction peak at $E_{pa} = 0.5$ V also disappears. These results were explained as the oxidation of the iron-centre of the ferrocenyl group at 0.48 V, followed by a chemical step [25]. When the free electron pair of phosphorus is involved in a chemical bond by either coordination to a Lewis acid or chemical oxidation to FcP(O)Ph₂, only one reversible ferrocenebased redox wave is observed, linking the chemical step to the phosphorus atom [25]. FcPPh₂, Fc₂PPh and Fc₃P were also more recently reinvestigated by Barrière and Geiger [26]. They established that medium effects play a significant role in the electrochemistry of these compounds. Their studies benefitted from utilizing CH_2Cl_2 and $[N(^nBu)_4][B(C_6F_5)_4]$ as solvent and electrolyte system because CH_2Cl_2 limit solvation processes while $[N(^nBu)_4]$ $[B(C_6F_5)_4]$ does not engage in ion pair formations as described above. Interestingly, in this regard, the electrochemistry of Fc(PPh₂)₂ was found to be dependent on solvent and electrolyte used in that $[N(^{n}Bu)_{4}][ClO_{4}]$ reacted with oxidation products [27]. Geiger and co-workers [26] also observed irreversible ferrocenyl redox couples and some follow-up chemical phosphorus activity. They also showed by occupying the free electron pair of the phosphine in a chemical bond as in the phosphine chalcogenides Fc₂PhP=O and Fc₃P=Se, reversible and resolved ferrocenyl redox couples may be obtained [26].

With this work we highlight different synthetic routes towards the monometallocenylphosphines, FcPPh₂, **1**, ruthenocenyldiphenyl phosphine, RcPPh₂, **2**, osmocenyldiphenylphosphine, OcPPh₂, **3**, and the positively charged compound diphenylphosphinocobaltocenium

hexafluorophosphate [Cc⁺PPh₂][PF₆⁻], **4**. We also report a comparison of the electrochemistry of these complexes and describe the crystal structure of **2**. By changing the metallocene metal centre, the phosphine cone-angle as well as the chemical stability of the catalyst may be influenced [20].

2. Experimental

2.1. General information

Solid reagents (Aldrich and Strem) were used without any further purification. Organic solvents were dried and distilled directly prior to use where specified. Doubly distilled water was used. Cyclopentadiene was prepared by cracking of dicyclopentadiene as described before [28]. Column chromatography was performed on Kieselgel 60 (Merck, grain size 0.040–0.063 nm) using hexane:diethyl ether (1:1) as mobile phase. [N(ⁿBu)₄][B(C₆F₅)₄] was synthesized utilizing a published procedure [29]. ¹H NMR spectra at 20 °C were recorded on a Bruker Advance DPX 300 NMR spectrometer at 300 MHz with chemical shifts presented as δ values referenced to SiMe₄ at 0.00 ppm utilizing CDCl₃ as solvent. The CDCl₃ was made acid free by passing it through basic alumina immediately before use. Elemental analysis was conducted by the Analytical Chemistry Section of the Chemistry Department of the UFS on a Leco TruSpec Micro instrument.

2.2. Synthesis

2.2.1. Ferrocenyldiphenylphosphine, FcPPh₂, 1

The previously published procedure by Sollott et al. was followed [22]. The workup was modified to decant the solution through filter paper after cooling. The remaining solids were washed with hot *n*-heptane (20 ml) and added to the *n*-heptane filtrate thereby removing all unreacted ferrocene. The remaining solids were washed with hot water (20 ml) in portions, followed by hot toluene (80 ml) in portions. The combined toluene solution was evaporated. The product was purified by repeated recrystallization from ethanol to yield 1.44 g (36%) of **1**, m.p. = 122 °C. Elemental analysis (%): calc. for C22H19FeP (370.2): C, 71.4; H, 5.2; found: C, 71.1; H, 5.0. ¹H NMR (CDCl₃, δ, ppm): 4.10 (s, 5H, C₅H₅); 4.13 (t, 2H, 0.5× C₅H₄, ³J_{HH} 1.84 Hz), 4.40 (t, 2H, 0.5× C₅H₄, ³J_{HH} 1.84 Hz); 7.37 (m, 10H, $2 \times C_6H_5$). ³¹P{¹H} NMR (CDCl₃, δ , ppm): -17 (s, P). ¹³C{¹H} NMR (CDCl₃, δ , ppm): 69 (s, C₅H₅); 71 (d, C₅H₄, ³J_{PC} 4 Hz); 73 (d, C₅H₄, ²J_{PC} 15 Hz); 76 (d, C_q/C₅H₄, ¹J_{PC} 6 Hz); 128 (d, C₆H₅, ³J_{PC} 7 Hz); 128 (s, C₆H₅); 134 (d, C₆H₅, ²J_{PC} 19 Hz); 140 (d, C_a/C₆H₅, ¹J_{PC} 9 Hz).

2.2.2. Ruthenocenyldiphenylphosphine, RcPPh₂, 2

Ruthenocene (1 g, 4.3 mmol) was dissolved in dry THF (15 ml) and the system degassed under Ar for 30 min. The solution was cooled to -78 °C and *t*-butyl lithium (2.55 ml, 4.3 mmol, 1 eq. Warning: t-butyl lithium combusts spontaneously upon air exposure) was added dropwise to the solution under Ar. The solution was allowed to warm to room temperature and stirred for 2 h. It was again cooled to -78 °C and chlorodiphenylphosphine (2.34 ml, 13.0 mmol, 3 eq.) was slowly added under Ar. The solution was allowed to warm to room temperature and stirred for a further 2 days. The reaction mixture was quenched with saturated sodium bicarbonate and extracted with CH₂Cl₂. The product was separated by column chromatography, ($R_f = 0.81$) to yield 0.34 g (19%) of **2**, m.p. = 127 °C. Recrystallisation of **2** from CH_2Cl_2 and *n*-hexane gave crystallographic quality crystals. Elemental analysis (%): calc. for C₂₂H₁₉RuP (415.4): C, 63.6; H, 4.6; found: C, 63.5; H, 4.6. ¹H NMR (CDCl₃, δ , ppm): 4.47 (s, 5H, C₅H₅); 4.50 (t, 2H, 0.5× C₅H₄, ³J_{HH} 1.61 Hz), 4.73 (t, 2H, 0.5× C₅H₄, ${}^{3}J_{HH}$ 1.65 Hz); 7.36 (m, 10H, 2× C_6H_5). ³¹P{¹H} NMR (CDCl₃, δ , ppm): -16 (s, P). ¹³C{¹H} NMR (CDCl₃, δ, ppm): 72 (s, C₅H₅); 73 (d, C₅H₄, ³*J*_{PC} 3 Hz); 75 (d, C₅H₄, ²*J*_{PC} 16 Hz); 80 (d, C_q/C₅H₄, ¹*J*_{PC} 9 Hz); 128 (d, C₆H₅, ³*J*_{PC} 7 Hz); 128 (s, C₆H₅); 133 (d, C₆H₅, ²*J*_{PC} 19 Hz); 139 (d, C_q/C₆H₅, ¹*J*_{PC} 10 Hz).

2.2.3. Osmocenyldiphenylphosphine, OcPPh₂, 3

OcPPh₂ was prepared from osmocene (0.3 g, 0.94 mmol) by following the same procedure as in the preparation of RcPPh₂, but by using dry ether (6 ml) instead of THF and by adding *n*-butyl lithium (0.6 ml, 1.1 mmol, 1.2 eq.) rather than *t*-butyl lithium. Chlorodiphenylphosphine (1.0 ml, 5.7 mmol, 5 eq.) was added and the product was separated by column chromatography, ($R_f = 0.79$) to yield 0.062 g (13%) of **3**, m.p. = 141 °C. Elemental analysis (%): calc. for C₂₂H₁₉OsP (504.6): C, 52.4; H, 3.8; found: C, 52.2; H, 3.7. ¹H NMR (CDCl₃, δ , ppm): 4.65 (m, 7H, C₅H₅, 0.5× C₅H₄); 4.91 (t, 2H, 0.5× C₅H₄, ³ J_{HH} 1.26 Hz), 7.38 (m, 10H, 2× C₆H₅). ³¹P{¹H} NMR (CDCl₃, δ , ppm): -14 (s, P). ¹³C{¹H} NMR (CDCl₃, δ , ppm): 66 (s, C₅H₅); 66 (d, C₅H₄, ³ J_{PC} 3 Hz); 68 (d, C₅H₄, ² J_{PC} 16 Hz); 73 (d, C_q/C₅H₄, ¹ J_{PC} 8 Hz); 128 (d, C₆H₅, ¹ J_{PC} 9 Hz).

2.2.4. Diphenylphosphinocobaltocenium hexafluorophosphate, [CcPPh₂][PF₆], **4**

The procedure published by Rudie et al. [20b] was modified by reducing the phosphine substituents from two to one, as follows: To a slurry of finely cut sodium wire (0.56 g, 24.4 mmol, 1 eq.) in THF (200 ml) at 0 °C and under N₂, freshly cracked cyclopentadiene [28] (2 ml, 24.4 mmol, 1 eq.) was slowly added, and the mixture stirred until all the sodium was consumed. The pink solution was cooled to -78 °C and chlorodiphenylphosphine (4.4 ml, 24.4 mmol, 1 eq.) was slowly added. The solution was allowed to warm to room temperature and stirred for 30 min. It was again cooled to -78 °C and again cyclopentadiene (2 ml, 24.4 mmol, 1 eq.) was added, followed by n-butyl lithium (24.3 ml, 48.7 mmol, 2 eq.). After 15 min of stirring, cobalt (II) bromide (5.32 g, 24.4 mmol) was added under a counter stream of N₂. The mixture was allowed to warm to room temperature and stirred for 16 h. Acetic acid (1.4 ml, 24.4 mmol, 1 eq.) was added and the mixture stirred in an open vessel for 15 min. The mixture was filtered, NH₄PF₆ was added to the filtrate and the solvent evaporated. The brown sludge was washed with warm *n*-hexane and from this, 7.3 g (58%) of **4** was crystallized from warm hexane, m.p. = 207 °C. Elemental analysis (%): calc. for C₂₂H₁₉CoP₂F₆ (518.3): C, 51.0; H, 3.7; found: C, 50.7; H, 3.6. ¹H NMR (CDCl₃, δ , ppm): 5.73 (s, 5H, C₅H₅); 5.91 (t, 2H, 0.5× $C_{5}H_{4}$, ${}^{3}J_{HH}$ 1.83 Hz), 6.13 (t, 2H, $0.5 \times C_{5}H_{4}$, ${}^{3}J_{HH}$ 1.68 Hz); 7.69 (m, 10H, 2× C₆H₅). ³¹P{¹H} NMR (CDCl₃, δ, ppm): 21 (s, P); 144 (m, PF6, J_{PF} 712 Hz). ¹³C{¹H} NMR (CDCl₃, δ, ppm): 86 (s, C₅H₅); 88 (d, C₅H₄, ${}^{2}J_{PC}$ 10 Hz); 88 (d, C₅H₄, ${}^{3}J_{PC}$ 8 Hz); 129 (d, C₆H₅, ${}^{2}J_{PC}$ 12.4 Hz); 131 (d, C₆H₅, ³*J*_{PC} 10 Hz); 133 (s, C₆H₅); C_q/C₆H₅ and C_q/C₅H₄ not observed).

2.3. Single crystal X-ray crystallography

Crystals of RcPPh₂, **2**, were obtained by slow evaporation of the solvents chloroform and *n*-hexane (1:1 mixture). A colourless single crystal, of dimensions $0.27 \times 0.12 \times 0.08 \text{ mm}^3$, was selected and used for data collection on a Bruker X8 ApexII 4K Kappa CCD diffractometer [30] with an exposure time of 10 s/frame collecting a total of 567 frames with a frame width of 0.5% covering up to $\theta = 28.28$ °to accomplish a 99.8% completeness. Frame integration and data reduction were performed using the software packages SAINT-Plus and XPREP [31]. Multi-scan absorption correction was performed on the data using SADABS [32]. The structure was solved by the direct methods software SIR97 [33] and refinement done with the WinGX [34] software package that includes SHELXL [35]. The non-hydrogen atoms were refined anisotropically. All H-atoms were positioned geometrically and refined using the riding model

with fixed C–H distances, for aromatic a C–H of 0.93 Å (CH) [U_{iso} (H) = 1.2 U_{eq}] and for methyl a C–H of 0.96 Å (CH) [U_{iso} (H) = 1.5 U_{eq}]. Molecular diagrams were drawn using the software package DIAMOND [36].

2.4. Electrochemistry

Measurements on *ca*. 1.0 mmol dm⁻³ solutions of the complexes in dry air free dichloromethane containing 0.10 mol dm⁻³ tetrabutylammonium tetrakis(pentafluorophenyl)borate, $[N(^{n}Bu)_{4}]$ $[B(C_6F_5)_4]$, as supporting electrolyte were conducted under a blanket of purified argon at 25 °C utilizing a BAS 100 B/W electrochemical workstation interfaced with a personal computer. A three electrode cell, which utilized a Pt auxiliary electrode, a glassy carbon working electrode (surface area 0.0707 cm²) and an inhouse constructed Ag/Ag⁺ (a silver wire, 0.01 mol dm^{-3} AgNO₃) reference electrode with vycor tip was used. Successive experiments under the same experimental conditions showed that all formal reduction and oxidation potentials were reproducible within 5 mV. Results are referenced against ferrocene, utilizing decamethyl ferrocene (Fc*) as internal standard. To achieve this, each experiment was first performed in the absence of ferrocene and decamethyl ferrocene, and then repeated in the presence of <1 mmol dm⁻³ decamethyl ferrocene. A separate experiment containing only ferrocene and decamethyl ferrocene was also performed. Data was then manipulated on a spreadsheet to set the formal reduction potentials of the FcH/FcH⁺ couple to 0 V. Under our conditions the Fc^*/Fc^{*+} couple was at -607 mV vs. FcH/FcH⁺, while the FcH/FcH⁺ couple was at 220 mV vs. Ag/Ag⁺. In CH₃CN/ 0.1 mol dm⁻³ [N(^{*n*}Bu)₄][PF₆], the Fc^{*}/Fc^{*+} couple was at -510 mV vs. FcH/FcH⁺ [37].

3. Results and discussion

3.1. Synthesis

The different reactivity of each parent metallocene necessitated different reaction conditions, or in the case of **4**, a completely different synthetic route to obtain each of the different metallocenylphosphines (Scheme 1). FcPPh₂ (**1**) was synthesized by Friedel Crafts reaction of ferrocene and chlorodiphenylphosphine, in the presence of AlCl₃ [22,23]. In our hands slightly better yields in shorter reaction times were obtained utilizing *n*-heptane (36%)



Scheme 1. Synthesis of metallocenylphosphines 1 (FcPPh₂), 2 (RcPPh₂), 3 (OcPPh₂) and 4, [CcPPh₂][PF₆].

as solvent due to its higher boiling point (98 °C) compared to nhexane as solvent (b.p. = 69 °C, with 31% yield). Purification of $\mathbf{1}$ required repeated recrystallization from ethanol. For RcPPh₂ (2) and $OcPPh_2$ (3), the metallocene first had to be lithiated, followed by reaction with chlorodiphenylphosphine. After column chromatography, low yields were obtained (19% and 13% respectively), but unreacted metallocene could be recovered. For **2**. ^{*t*}BuLi has to be the lithiating reagent because ⁿBuLi leads to di-lithiated products, even in stoichiometric ratios. For osmocene, monolithiation was achieved utilizing ^{*n*}BuLi as inferred from the isolation of pure **3**, while no Oc(PPh₂)₂could be isolated. Compound **4** required a different synthetic approach, since it is not possible to lithiated the oxidised form of cobaltocene. For 1, 2 and 3, the Fe, Ru and Os metal centres are all in the +2 oxidation state which results in a neutral metallocene. Complex **4** exists as a cationic species, due to the cobalt centre being in the +3 oxidation state. To obtain 4, cyclopentadiene was first derivatized to cyclopentadienyldiphenylphosphine, Scheme 1. After addition of an equal amount of unsubstituted cyclopentadiene, complexation with CoBr₂ led to a mixture of cobaltocenium, diphenylphosphinocobaltocenium, 4, and 1,1'bis(diphenylphosphino)cobaltocenium hexafluorophosphate $[(dppc)^+(PF_6)^-]$ [20b]. These three products could conveniently be separated from each other by recrystallization in *n*-hexane.

3.2. Single crystal X-ray structure of 2

Crystallographic quality crystals of RcPPh₂, **2**, were obtained from CH₂Cl₂ and n-hexane by slow evaporation. The compound crystallized in the monoclinic space group $P2_1/c$. Fig. 1 shows the molecular structure of **2** highlighting atom labelling. Selected bond lengths (Å) and angles (°) are summarized in the caption. Crystal data and refinement parameters are summarized in Table 1.



Fig. 1. Molecular structure of RcPPh₂, **2**, showing atom labelling. Displacement ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (°) are: C(1)–P 1.812(3), C(11)–P 1.832(2), C(21)–P 1.836(2), C(1)–C(2) 1.438(3), C(2)–C(3) 1.418(4), C(3)–C(4) 1.417(4), C(4)–C(5) 1.421(3), C(1)–C(5) 1.441(3), C(11)–C(12) 1.387(3), C(11)–C(16) 1.393(3), C(21)–C(22) 1.391(3), C(21)–C(26) 1.376(3); C(11)–P–C(11) 102.35(10), C(1)–P–C(21) 102.46(11), C(11)–P–C(21) 102.070(10), C(11)–C(12)–C(23) 120.9(2), C(11)–C(26)–C(25) 120.7(2), C(12)–C(21)–C(26) 118.3(2).

Complex **2** exhibits a distorted pyramidal geometry around the P atom with C(11)–P–C(21) being the smallest at 100.70(10)°. The C(1)–P bond from the ruthenocene group to the phosphorus atom is 1.8129(3) Å and 0.022 Å shorter than the distance between the phosphorus atom and the C-atom of the phenyl groups bonded to it. This indicates a stronger bond between the ruthenocene group and the P atom compared to bonds to the phenyl rings due to the better electron-donating capabilities of the ruthenocenyl groups. A convenient measure of the electron-donating capability of groups are Gordy scale group electronegativities, χ_R , with $\chi_{R=Rc} = 1.99$ (most electron-donating) and $\chi_{R=Ph} 2.21$ (relatively more electron withdrawing) [38]. The same bond length tendency was also observed in the crystal structure of FcPPh₂, **1**. The corresponding distance between the phosphorus atom and the ferrocenyl group in **1** was 1.810(1) Å [39] ($\chi_{R=Fc} = 1.87$ [38].

The average C–C bond length and bond angle in the phenyl rings are 1.384 Å and 120.3° respectively and compares well with literature values [20a,39,40]. The average C–C bond distance in the aromatic P-substituted cyclopentadienyl ring (1.427(4) Å) is 0.021 Å longer than the average C-C bonds in the unsubstituted cyclopentadienyl ring (1.406(5) Å). This can be ascribed to donation of electron density from the ruthenocenyl group towards the P atom which decreases the P-C_{Rc} bond length but increases the C-C bond lengths in the ring. For FcPPh₂ (1) [39] and other metallocene derivatives [41], the difference in cyclopentadienyl C–C bond lengths was found to be 0.01 Å. The cyclopentadienyl rings of 2 were found to deviate 7.50° from the eclipsed conformation. The dihedral angle between the planes formed by the cyclopentadienyl rings is approximately 0.6°. They are separated by a centroid-to-centroid distance of 3.627 Å, which falls between the values for free ruthenocene (3.68 Å) [20a], and 1,1'-bis(diphenylphosphino)ruthenocene, Rc(PPh₂)₂ (3.606 Å) [42].

3.3. Electrochemistry

The cyclic voltammetry of free ferrocene, ruthenocene, osmocene and cobaltocenium hexafluorophosphate has been well

Table 1Crystal data and structural refinement summary for RcPPh2 2.

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Empirical formula	C ₂₂ H ₁₉ PRu	θ range for data collection/deg	2.41-28.00		
Molecular weight	415.41	Max. and min. transmission	0.9251 and 0.7761		
Temperature/K	100(2)	Reflections collected	50,798		
Wavelength/Å	0.71073	Independent reflections	4221 [<i>R</i> (int) = 0.0360]		
Crystal system	Monoclinic	Completeness to $\theta = 28.00^{\circ}$	100.0%		
Space group	P2(1)/c	Absorption correction	None		
Unit cell dimensions/Å	a = 14.2986(7) b = 10.4474(5) c = 11.6886(6)	Index ranges	$-18 \le h \le 18$ $-13 \le k \le 13$ $-15 \le l \le 15$		
Volume/Å ³	1745.30(15)	Refinement method	Full-matrix least- squares on F ²		
Ζ	4	Data/restraints/ parameters	4221/0/217		
Density (calculated)/ Mg/m ³	1.581	Goodness- of-fit on F ²	1.072		
Absorption coefficient	0.989 mm^{-1}	Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0275, wR2 = 0.0710		
F(000)	840	R indices (all data)	R1 = 0.0320, wR2 = 0.0741		
Crystal size/mm ³	$0.27\times0.12\times0.08$	Largest diff. peak and hole/e Å ⁻³	1.520 and -0.498		



Fig. 2. Cyclic voltammograms of 1 mmol dm⁻³ solutions of pure PPh₃, as well as a mixture of all metallocenes used in this study in the same solution, and compounds **1**, **2**, **3** and **4**, in dichloromethane containing 0.1 mol dm⁻³ [N(ⁿBu)₄][B(C₆F₅₎₄] at 100 mV s⁻¹ on a glassy-carbon working electrode and at 25 °C. Linear sweep voltammetric curves at 2 mV s⁻¹ of phosphines **2**, **3** and **4** (in acetonitrile) are shown below the CV of the compound. The insert above the CV of **4** shows phosphine oxidation peaks P₁ and P₂ in acetonitrile containing 0.1 mol dm⁻³ [N(ⁿBu)₄][PF₆] at 100 mV s⁻¹. For compounds **1**, **2**, and **3**, the dotted lines indicate scans reversed at various potentials. The peak labelled Fc⁺ is that of decamethyl ferrocene, which was used throughout as an internal standard.

documented [13,17,43]. For comparative purposes the CV of these four metallocenes mixed together in the same CH_2Cl_2 solution containing 0.1 mol dm⁻³ [N(ⁿBu)₄][B(C₆F₅)₄] is shown in Fig. 2. Relative to FcH/FcH⁺, the very reactive cobaltocenium anion, [CcH]⁻ undergoes poorly resolved but reversible oxidation to the neutral Co^{II} species at $E^{0'} = -2.37$ V. In acetonitrile containing $[N(^{n}Bu)_{4}][PF_{6}]$ this peak is detected at -2.46 V. The $[CcH]^{+}/[CcH]^{0}$ electrochemical reversible redox process is at $E^{0'} = -1.324$ V vs FcH/ FcH⁺. The electrochemical reversible decamethyl ferrocene, Fc^{*}, and ferrocene couples are under the conditions of the CV in Fig. 2 at $E^{0'} = -601$ mV and 0 mV respectively, although when Fc^{*} and Fc were the only analytes in solution, $E^{0'}(Fc^*) = -608 \text{ mV } vs \text{ FcH/FcH}^+$ [37]. Osmocene and ruthenocene showed $E^{0} = 389 \text{ mV}$ and 523 mV vs FcH/FcH⁺ respectively for the $[OcH]^{+/0}$ and $[RcH]^{+/0}$ couples [44]. When ruthenocene is scanned in the presence of only decamethyl ferrocene, additional weak cathodic peaks at approximately -300 mV and 100 mV are observed at T = 250 K or 298 K respectively and are associated with two separate ruthenocenium dimers [13]. In all cases, ΔE_p < 88 mV at a slow (100 mV s⁻¹) scan rate except the $[CcH]^{0/-}$ couple which showed $\Delta E_{\rm p} = 123$ mV under the conditions of the scan shown 2nd from the top in Fig. 2.

The electrochemistry of phosphines **1–4** has been studied in detail. Results at a scan rate of 100 mV s⁻¹ are summarised in Table 2 while selected CV's are shown in Figs. 2 and 3. Supplementary data contains electrochemical data at scan rates 100, 200, 300, 400 and 500 mV s⁻¹.

The electrochemistry of [Cc⁺PPh₂][PF₆], **4**, in CH₂Cl₂/[N(ⁿBu)₄] $[B(C_6F_5)_4]$, like free cobaltocene, showed two reversible oneelectron transfer waves, Figs. 2 and 3. The wave labelled $Cc^{-/0}$ at $E_{pc}=-2.176~(E^{0\prime}=-2.122$ V, $\Delta E_p=$ 108 mV at 100 mV s^{-1}) represents the reduction of the Co^{II} core of cobaltocene to a Co^{I} species and showed less electrochemical reversibility than the $Cc^{-/0}$ couple of **4** (Table 2). Chemical reversibility of the $Cc^{-/0}$ couple was good with $i_{pa}/i_{pc} = 0.89$. Electrochemical and chemical reversibility is characterised by $\Delta E = 59$ mV and $i_{pa}/i_{pc} = 1$ respectively as described elsewhere [45]. The second peak labelled $Cc^{0/+}$ is much more ideal in appearance. The electrochemically and chemically reversible reduction of Co^{3+} to Co^{2+} was observed at $E^{0} = -1.062$ V, with $\Delta E_{\rm p} = 86$ mV and $i_{\rm pa}/i_{\rm pc}$ approaching 1 at slower scan rates. Incorporation of the PPh₂ substituent as part of the compound structure in phosphine 4 caused the formal reduction potentials of the cobaltocenium fragment to be shifted to more positive values by $\Delta E^{0'} = \Delta E^{0'}_{4} - \Delta E^{0'}_{free Cc} = 254 \text{ mV}$ and 263 mV relative to free cobaltocenium hexafluorophosphate for the Co^{II/I} and Co^{III/II} redox couples respectively. This implies that the PPh₂ substituent decreased the electron density on the Co^{1+} , Co^{2+} and Co^{3+} centres of 4. The phosphorus oxidation of 4 falls outside of the potential window of CH₂Cl₂ as solvent, Figs. 2 and 3. For this reason, the electrochemistry of **4** was repeated in CH₃CN/[N(ⁿBu)₄][PF₆]. This allows observation of the phosphorus oxidation at the solvent potential limit, Fig. 3.

Table 2

Cyclic voltammetric data at 100 mV s⁻¹ (potentials vs. FcH/FcH⁺) of *ca*. 1 mmol dm⁻³ solutions of **1–4** in CH₂Cl₂^a containing 0.1 mol dm⁻³ [N(ⁿBu)₄][B(C₆F₅)₄] supporting electrolyte at 25 °C.

Compound	Wave	$E_{\rm pa}\left({\sf V}\right)$	$E^{\mathbf{o}_{\prime}}\left(V\right)$	$\Delta E_{\rm p} ({\rm mV})$	<i>i</i> _{pa} (μA)	$i_{ m pc}/i_{ m pa}$	Wave	$E_{\rm pa}\left({\sf V}\right)$	i _{pa} (μA)	Wave	$E_{\rm pa}\left({\sf V}\right)$	i _{pa} (μA)
4 : $[Cc^+PPh_2]^b$	Cc ^{-/0}	-2.176	-2.122	108	0.54	0.89						
4: [Cc ⁺ PPh ₂] ^b	Cc ^{0/+}	-1.105	-1.062	87	0.50	0.99	P ₁ ^{c,d}	1.136 ^d	0.70 ^d	$P_2^{c,d}$	1.370 ^d	2.43 ^d
1: FcPPh ₂	Fc ^{0/+}	0.117	0.078	76	0.55	0.99	P ₁	1.128	0.25 ^e	P ₂	1.441	0.56 ^e
3: OcPPh ₂	$Oc^{0/+}$	0.355	0.224	262	0.70	0.31 ^f	P ₁	0.893	0.36	P ₂	1.090	0.86
2: RcPPh ₂	Rc ^{0/+}	0.476	0.362	229	0.17	< 0.15 ^f	P ₁	0.754	0.07 ^e	P ₂	1.160	0.18 ^e

^a Supplementary data provide details for **1** and **4** in CH₃CN/0.1 mol dm⁻³ [N(^{*n*}Bu)₄][PF₆].

^b Counter anion is PF₆.

^c Wave P₁ represents oxidation of Mc⁺Ph₂P;, wave P₂ represents electrochemical oxidation of either Mc⁺Ph₂P⁺⁺ or its chemically decomposed product.

^d No peaks observed in $CH_2Cl_2/0.1 \text{ mol } dm^{-3} [N(^nBu)_4][B(C_6F_5)_4]$, data provided are for experiments in $CH_3CN/0.1 \text{ mol } dm^{-3} [N(^nBu)_4][PF_6]$.

^e Peak currents of waves P_1 and P_2 are smaller than that of wave $F_c^{0/+}$ because of the irreversible nature and broadness of the peaks. It follows that the size of i_{pa} for waves P_1 and P_2 has no analytical meaning as the size of i_{pa} for the $F_c^{0/+}$ couple has. The LSV did confirm the correct number of electrons was transferred at wave P_1 . The same applies to waves P_1 and P_2 of **2**.

^f Peak cathodic currents were very weak for these electrochemical reversible processes, probably because the fast rate of destruction of the unstable 17 electron Rc⁺ and Oc⁺ species in the presence of the phosphine group.



Fig. 3. Effect of $CH_2Cl_2/0.1 \text{ mol } dm^{-3} [N(^nBu)_4][B(C_6F_5)_4] (CV at 500 mV s^{-1}) or <math>CH_3CN/0.1 \text{ mol } dm^{-3} [N(^nBu)_4][PF_6] (CV's at 100, 200, 300, 400 and 500 mV s^{-1}) as solvent and electrolyte on redox processes of 1 mmol <math>dm^{-3}$ solutions of **1**, FcPPh₂, and **4**, [CcPPh₂] [PF₆], on a glassy-carbon working electrode and at 25 °C. The top CV is that of pure PPh₃ in $CH_2Cl_2/0.1 \text{ mol } dm^{-3} [N(^nBu)_4][B(C_6F_5)_4] at 100 mV s^{-1}$. The peak labelled Fc* is that of decamethyl ferrocene, which was used throughout as an internal standard.

In CH₃CN, the cobalt reduction peaks exhibit similar ΔE_p and i_{pa}/i_{pc} values to that in CH₂Cl₂ (Supplementary data). Two phosphorus peaks, P₁ and P₂ are clearly visible. Peak P₁ at 1.136 V appears as a shoulder on peak P₂ at 1.370 V at 100 mV s⁻¹, see Figs. 2 and 3. Peak P₁ is interpreted as a one electron oxidation of the phosphine functional group at the free electron pair; the LSV of this peak shows it to involve the same number of electrons as the two cobalt waves, Fig. 2. The second phosphorus-related oxidation is interpreted to involve electrochemical oxidation of the Cc⁺Ph₂P⁺⁺ radical cation product, Scheme 2, or of a chemically decomposed form of this species. $E^{0'}$ of the [CcPPh₂]^{0/+} couple (at far negative potentials) was within *ca*. 100 mV of each other in the two solvent systems, while for the [CcPPh₂]^{0/+} couple, $E^{0'}$ shifted by 33 mV from -1.062 V (CH₂Cl₂) to -1.095 V (CH₃CN).

The phosphorus related peaks P_1 and P_2 were not observable in $CH_2Cl_2/[N(^nBu)_4][B(C_6F_5)_4]$, but they were detected in $CH_3CN/[N(^nBu)_4][PF_6]$ at 1.136 and 1.370 V respectively.

The CV's of ferrocenyldiphenylphosphine in CH₂Cl₂/[N(^{*n*}Bu)₄] [B(C₆F₅)₄] exhibited, similar to what was observed during previous studies, an anodic wave for the oxidation of the ferrocenyl Fe^{II} centre at $E_{pa} = 0.117$ V followed by two irreversible oxidation



Scheme 2. Schematic representation of electrochemical reactions of metallocenecontaining phosphines $FcPPh_2$ **1**, $RcPPh_2$ **2**, $OcPPh_2$ and $[CcPPh_2)][PF_6]$ **4**. Wave P_2 involves either electrochemical oxidation of M^{III} $Cp(C_5H_4P^{\star+}Ph_2]^+$ or of its chemical decomposition product.

waves at 1.128 V and 1.441 V (peaks labelled P_1 and P_2) due to oxidation at the phosphorus centre, Figs. 2 and 3 [24–26]. Wave P_1 appears as a low current-intensity shoulder on P_2 . Linear sweep voltammetry (LSV) shows the number of electrons transferred during oxidations at waves $Fc^{0/+}$ and P_1 are equal (Fig. 2), namely one. This result is consistent with peak P_1 representing a oneelectron oxidation of the phosphorus lone-pair of (Fc⁺Ph₂P⁺) to liberate the radical cation Fc⁺Ph₂P⁺⁺. Either Fc⁺Ph₂P⁺⁺ or its chemically decomposed products undergoes further oxidation at peak P_2 (1.441 V). Neither of the two phosphine peaks shows any electrochemical reversibility.

The cathodic waves Fc_{red1} and Fc_{red2} associated with ferrocenyl group reduction (Figs. 2 and 3) provide additional insight to the electrochemical profile of 4. When the scan direction is reversed at potentials small enough to exclude wave P_1 , the $Fc^{0/+}$ couple show electrochemical reversibility with $E^{0\prime} = 0.078$ V vs. FcH/FcH⁺, $\Delta E_{\rm p} = E_{\rm pa} - E_{\rm pc} = E_{\rm pa} - E_{\rm Fc, red1} = 116 - 40 = 76$ and $i_{\rm pc}/i_{\rm pa} = 0.99$. However, at fast scan rates (\geq 300 mV s⁻¹), and if the reversal potential is large enough to include wave P₁, wave E_{Fc.red1} is not any more observable. It has been replaced by the ferrocenium reduction wave Fc_{red2} at *ca*. 0.476 V (Figs. 2 and 3). At slow (100 mV s⁻¹) scan rates utilizing potential ranges wide enough to include wave P1, both reduction waves Fc_{red2} and Fc_{red1} , are observed. Cathodic wave Fc_{red2} leads to $\Delta E_p = E_{pa} - E_{Fc,red2} = 116 - 476 = -360$ mV. Cathodic wave Fcred2 is therefore not assigned to reduction of the ferrocenium group of Fc⁺PPh₂. It probably belongs to the reduction of the ferrocenium group of a species that was generated during (or directly after) phosphorus oxidation at peak P₁. This new species survives long enough to detect ferrocenium reduction at wave Fc_{red2}. The electronic properties of this new species causes the ferrocenium group to be much more electron deficient than in Fc^+PPh_2 and resulted in ferrocenium reduction to move from $E_{pc} = 40 \text{ mV} (Fc_{red1})$ to 0.476 V (wave Fc_{red2}). In the wide scan, at slow scan rates (100 mV s⁻¹), the origin of reduction peak Fc_{red1} can be attributed to the diffusion of yet unoxidised molecules of 1 from the bulk of the solution to the electrode surface (i.e. which have not undergone phosphine oxidation, but which have undergone ferrocenyl oxidation) while the applied potential decreased from ca. 0.7 V to ca. 0.04 V. Incorporation of the ferrocenyl group as part of the phosphine ligand caused the formal oxidation potential of this metallocene to be observed at a potential 78 mV more positive than free ferrocene, which implies the PPh₂ group withdraws electron density from the ferrocenyl group. Electrochemical reactions summarizing the above redox processes are shown in Scheme 2.

The electrochemistry of 1 was also studied in CH₃CN and [N(ⁿBu)₄][PF₆] as solvent and supporting electrolyte system. Peaks P_1 and P_2 were more clearly identifiable, as shown in Fig. 3. The same redox processes as in the case of CH₂Cl₂ as solvent was observed but all redox processes were slightly shifted to different potentials compared to the CH₂Cl₂ result. Ferrocenyl oxidation was observed at $E_{pa} = 0.139$ V (anodic peak of wave $Fc^{0/+}$, at 100 mV s⁻¹), followed by an irreversible oxidation wave at 1.052 V, wave P₁, due to phosphorus oxidation, as well as an oxidation wave at 1.436 V (wave P₂). When the switching potential was such that phosphorus oxidation at wave P1 does not commence, the ferrocenyl oxidation is chemically reversible with $E^{0} = 0.105$ V, $\Delta E = 67$ mV and $i_{pc}/i_{pa} = 0.99$ at 100 mV s⁻¹ scan rate. This is about 30 mV larger than that observed in CH₂Cl₂. The source of peak Fc_{red1} in the wide scan to include waves P1 and P2 at slow scan rates is again due to diffusion of 1 from the bulk of the solution while the potential decreased from ca. 0.700 V to peak Fcred1. The reduction wave Fc_{red2} was observed at the higher potential of 0.189 V (rather than the expected 0.071 V of wave Fc_{red1}). Observation of this wave is again due to the reduction of the ferrocenium group of a species that was generated during (or directly after) phosphorus oxidation at peak P₁. Reversing the scan before peak P₂ commences caused no change in the observation of wave $\ensuremath{\mathsf{Fc}_{red2}}$ which indicates that peak P₂ does not influence the reduction reaction associated with peak Fc_{red2}. The redox processes of **1** in CH₃CN are thus also consistent with the electron-transfer reactions shown in Scheme 2 although each redox process occurred at lower potentials than that observed in $CH_2Cl_2/[N(^nBu)_4][B(C_6F_5)_4]$.

RcPPh₂, **2**, and OcPPh₂, **3**, show very similar CV's compared to **1** (Fig. 2), but they differ in terms of metal reversibility during electrochemical processes. Both show three irreversible oxidation peaks. Oxidation of the metallocene centre was observed at waves Oc^{0/+} and Rc^{0/+} respectively and does not show electrochemical or chemical reversibility. The lack of pronounced Rc⁺ or Oc⁺ reduction peaks is probably due to the instability of the 17e⁻ ruthenocenium and osmocenium centres. No dimeric ruthenocene species, as reported before [13] for free ruthenocene could be observed in the reduction waves of 2 and 3. It is very likely that the two metallocenium species Rc^+ and Oc^+ are destroyed faster than Fc^+ by internal electron transfer from the free electron pair on the phosphine group, just as the oxidised RcH⁺ cation radical of free ruthenocene is destroyed by any nucleophilic or electron donating species [13]. The phosphine-bound osmocenyl group underwent oxidation (Fig. 2) at a potential of $E_{pa} = 0.355$ V. This is 73 mV smaller (more negative) than that of free osmocene in CH₂Cl₂ at 100 mV s⁻¹. The phosphine bound ruthenocenyl group was oxidized at an E_{pa} value of 127 mV more negative than free ruthenocene. These lowering in potentials imply that in the case of 2 and **3**, the PPh₂ group donates electron density to the ruthenocenyl and osmocenyl groups, directly opposite to what was found for the iron and cobalt derivatives, 1 and 4. This tendency is following the trend set in ease of metal oxidation from the M^{II} to M^{III} state. The Co and Fe complexes 4 and 1 have the lowest redox potentials at -1.062 and 0.078 V respectively. The Os and Ru complexes 3 and **2** exhibited these redox processes at much larger potentials: 0.224 and 0.362 V vs. FcH/FcH⁺ respectively, Table 1. Because the measured potentials are also a function of the group electronegativity of the metallocenes (i.e. its capability to donate or withdraw electrons to or from a molecule) [38,45a], it is clear that in the case of **2** and **3**, which exhibits larger redox potentials, the metallocenyl groups could act as electron-withdrawing agents relative to the PPh₂ functionality. This electron donation from PPh₂ to metallocenyl would lower the metallocenyl redox potential. In the case of **1** and **4**, the metallocenes acts as electron-donating groups relative to PPh₂. In donating electron density to the PPh₂ group, the redox potential of **1** and **4** is increased.

For **2** and **3**, wave P_1 is, as in the case of FcPPh₂, associated with oxidation on the phosphorus centre, and peak P_2 with oxidation of oxidised products. The overall reaction sequence is summarized in Scheme 2. The LSV indicates the number of electrons transferred during metallocene oxidation (at waves $Rc^{0/+}$ and $Oc^{0/+}$) and phosphine oxidation at wave P_1 are equal and one.

4. Conclusions

The synthesis of the metallocene-containing monophosphine series $FcPPh_2$ (1), $RcPPh_2$ (2), $OcPPh_2$ (3) and $[Cc^+PPh_2][PF_6]$ (4) from PPh₂Cl highlighted differences in reactivity of each metallocene. Ferrocene could react with PPh₂Cl by a Friedel Crafts procedure in the presence of AlCl₃ to liberate **1**. Ruthenocene required lithiation with ^tBuLi to prevent formation of di-lithiated ferrocene and subsequently also Rc(PPh₂)₂. RcLi was then reacted with PPh₂Cl to obtain 2. For osmocene, monolithiation was achieved with a 1.2 equivalent addition of ⁿBuLi. Subsequent reaction with PPh₂Cl liberated pure **3** and no Oc(PPh₂)₂ could be isolated. For the synthesis of 4, phosphination of cationic cobaltocenium hexafluorophosphate proved to be impossible. Derivatisation of free cyclopentadiene prior to complexation with Co^{III} to form $[Cc^+PPh_2]$ [PF₆], **4**, was needed. The ruthenocene complex **2** crystallizes in the monoclinic space group $P2_1/c$ and the Cp rings deviated 7.5° from the eclipsed conformation. A detailed study of the electrochemistry of these mono metallocenvldiphenvlphosphines showed the traditional metallocenyl^{0/+} couple in the following order: Cc⁺ (**4**, reversible, $E^{0'} = -1.062 \text{ V}$ < Fc (1, reversible, $E^{0'} = 0.078 \text{ V}$ < Oc (3, irreversible, $E_{pa} = 0.355 \text{ V}$ < Rc (**2**, irreversible, $E_{pa} = 0.476 \text{ V}$). For **1** and **4**, the metallocenyl E^{0} was larger than that of the parent free metallocene, which indicated the PPh₂ group in FcPPh₂ and [Cc⁺PPh₂][PF₆] removes electron density from these metallocenyl groups. In contrast, in OcPPh₂ and RcPPh₂, the PPh₂ behaved as an electron-donating group which increased the electron density of the Rc and Oc groups. This lowered the oxidation potentials of 2 and 3 relative to the parent metallocene. [Cc⁺PPh₂][PF₆] also showed a quasi-reversible $Cc^{-/0}$ couple at -2.122 V vs FcH/FcH⁺. This potential is 254 mV more positive than that observed for the parent metallocene, [Cc⁺][PF₆]. Finally, two separate irreversible phosphorus oxidation peaks, P1 and P2 were identified. The first, at $E_{pa} > 0.754$ V, corresponds to a one-electron oxidation of the free electron-pair on the phosphorus atom to generate the radical cation Mc⁺Ph₂P^{•+}. The second at $E_{pa} > 1.090$ V relates to electrochemical oxidation of the radical cation and/or its chemical decay products.

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Appendix A. Supplementary material

CCDC 953336 contains 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.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.12.027.

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