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PII: S0022-328X(16)30026-2

DOI: 10.1016/j.jorganchem.2016.01.026

Reference: JOM 19377

To appear in: Journal of Organometallic Chemistry

Received Date: 5 October 2015

Revised Date: 19 January 2016

Accepted Date: 21 January 2016

Please cite this article as: M.S. Inkpen, A.J.P. White, T. Albrecht, N.J. Long, Complexes comprising 'dangling' phosphorus arms and tri(hetero)metallic butenynyl moieties, *Journal of Organometallic Chemistry* (2016), doi: 10.1016/j.jorganchem.2016.01.026.

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Complexes comprising 'dangling' phosphorus arms and tri(hetero)metallic butenynyl moieties

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ABSTRACT: *Trans*-RuCl₂(PP₃)₂ (**1a**) (PP₃ = tris[2-(diphenylphosphino)ethyl]phosphine) was prepared by reaction of RuCl₂(PPh₃)₃ with 2 eq. PP₃. Through coordination of two potentially tetradentate ligands in a bidentate arrangement, four uncoordinated phosphine moieties remain readily available for subsequent reaction. This is demonstrated through their facile oxidation with hydrogen peroxide, providing *trans*-RuCl₂(PP[P=O]₂)₂ (**1b**) (PP[P=O]₂ = bis[2-(diphenylphosphine oxide)ethyl][2-(diphenylphosphino)ethyl]phosphine). Whilst chloride abstraction reactions from **1a** appear slow (typical for *trans* dichlorides), *cis*-RuCl₂(PP₃) is shown to react rapidly with ethynylferrocene under 'Dixneuf' conditions (CH₂Cl₂, NaPF₆, NEt₃), providing the tri(hetero)metallic butenynyl complex [(PP₃)Ru(η³-FcC₃CHFc)]PF₆ (**2**, Fc = ferrocenyl). The pendant groups of **1a-b** offer great potential for future coordination studies (for example, to prepare mixed transition metal/lanthanide materials), whereby the facile synthetic route to **2** suggests a path towards examination of complex mixed-valence systems comprising multiple redox-active centres.

1. INTRODUCTION

The functionalization of identical groups within the same molecule poses a particular synthetic challenge, typically requiring multi-step processes involving protecting groups, or inelegant (and often low yielding) stoichiometric control. New strategies for different substrates are therefore of interest, facilitating the preparation of asymmetric systems for catalysis and materials science. For mixed phosphine-phosphine oxides (a hemilabile ligand class, comprising both 'hard' and 'soft' nucleophilic groups),[1] one successful approach has been to coordinate a multidentate phosphine to a metal centre in such a way so as one or more of the phosphine groups remain uncoordinated. The latter can then be selectively oxidized to the phosphine oxide (or indeed subjected to alternative reactions). The 'soft' pendant groups in such materials have been shown to bind to a range of metal centres, forming discreet or polymeric heterometallics (transition metal-lanthanide).[2-5]

Such a strategy first requires generation of a starting complex with 'dangling' arms (NB. the mixed phosphinephosphine oxide ligand remains on the same specific metal centre unless a strategy is devised to displace it). Polydentate ligands (>3 binding groups) are of particular interest in this context, finding widespread utility in homogenous catalysis to enforce specific geometries at a metal centre or confer enhanced stability through the chelate effect.[6] However, in the specific case of incompletely coordinated tripodal phosphines with a 1:2 metal to ligand ratio, few examples have been reported. These include Mo(PP₃)₂[7] and MX₂(L)₂ (M = Pt, Pd; L = PP₃, tris[2-(diphenylphosphino)ethyl]amine; X = Cl, Br, I, NO₃)[8] (Figure 1). A new addition to this select group, RuCl₂(PP₃)₂ (**1a**), is reported here. We show that its four uncoordinated –PPh₂ groups may indeed be subjected to further reaction – treatment with H_2O_2 readily converting the latter to $-P(O)Ph_2$ (1b) (Scheme 1, right).



Figure 1. Previously reported mononuclear complexes with incompletely coordinated tripodal phosphines and a 1:2 metal to ligand ratio (P' = PPh₂; M = Pt, Pd; A = P, N; X = Cl, Br, I, NO₃).



Scheme 1. Synthesis of $\operatorname{RuL}_2(\operatorname{PP}_3)_n$ (*n* = 1, 2) complexes.

Noting also the reversible redox behavior of the RuL_2P_4 (L = anionic ligand, P = phosphine) family, we characterized **1a** and the related [(PP₃)Ru(η^3 -FcC₃CHFc)]PF₆ (**2**) complex

(Scheme 1, left) using solution voltammetry. Though ferrocenyl-terminated butenynyl complexes similar to **2** are known – for example, with coordinated $(\eta^5-C_5Me_4H)_2Ti[9]$, $Cp(PR_3)Ru$ (R = Me, Ph, Cy)[10], $Cp_2Ti[11]$ moieties – these have seldom[11] been subjected to electrochemical studies.

2. EXPERIMENTAL

2.1 Conditions and materials

All preparations were carried out using standard Schlenk line and air-sensitive chemistry techniques under an atmosphere of nitrogen. No special precautions were taken to exclude air or moisture during workup, unless otherwise stated. Solvents used in reactions were sparged with nitrogen and dried with alumina beads, Q5 Copper catalyst on molecular sieves, or 3A molecular sieves,[12] where appropriate. Silica and neutral alumina of Brockmann activity I (0% H₂O) or II (3% H₂O) were used for chromatographic separations. RuCl₂(PPh₃)₃[13] and RuCl₂(PP₃)[14] (method B) were prepared via literature methods from commercially available starting materials. All other materials were purchased from commercial suppliers and used without further purification.

2.2 Instrumentation

Unless otherwise stated, ${}^{1}H$, ${}^{13}C{}^{1}H$, ${}^{31}P{}^{1}H$ and ${}^{19}F$ NMR spectra were recorded at ambient temperature on Bruker 400 or 500 MHz spectrometers and internally referenced to the residual solvent peaks of CDCl₃ at δ 7.26 (¹H) and 77.16 ppm $({}^{13}C{}^{1}H{})[15]$ or externally to 85% phosphoric acid or CFCl₃ (0.00 ppm). $^{13}C{^1H}$ spectra were assigned where possible using 2D heteronuclear correlation experiments. UV-vis and IR spectra were recorded on a PerkinElmer LAMBDA 25 UV/vis spectrophotometer or a PerkinElmer Spectrum 100 FT-IR spectrometer, respectively. Mass spectrometry analyses were conducted by the Mass Spectrometry Service, Imperial College London. Microanalyses were carried out by Stephen Boyer of the Science Centre, London Metropolitan University. Cyclic voltammograms were recorded under an atmosphere of argon in CH₂Cl₂/0.1 M "Bu₄NPF₆ on a CHI760C potentiostat (CH Instruments, Austin, Texas) with a glassy carbon disc as working electrode (diameter = 2.5 mm), and Pt-wire as reference and counter electrodes respectively. Analyte solutions were between 0.1-1 mM. Potentials are reported relative to $[FeCp_2]^+/[FeCp_2],$ measured against internal an [FeCp*2]+/[FeCp*2] reference.

2.3 Synthetic Details

2.3.1 Trans-RuCl₂(PP₃)₂ (1a)

A solution of RuCl₂(PPh₃)₃ (0.150 g, 0.123 mmol) and PP₃ (0.214 g, 0.319 mmol) in toluene (1 mL) was heated in an oil bath at 120°C for 2 h. After cooling, the toluene solution was filtered through cotton wool into a clean glass vial, using CH₂Cl₂ (3 mL) to extract residual material from the reaction flask. Diethyl ether (20 mL) was layered above the toluene/CH₂Cl₂ solution, forming yellow crystals after 6 d. The solution was decanted, the solid material washed with diethyl ether (1 x 15 mL) and acetone (1 x 15 mL) and dried in vacuo to provide 1 as a yellow-orange powder (0.133 g, 71%). Crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a CH₂Cl₂ solution. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 1.45 (br m, 4H, CH₂), 1.77 (br m, 12H, CH₂), 1.94 (br m, 4H, CH₂), 2.53 (br m, 4H, CH₂), 6.98 (t, J = 7.6 Hz, 8H, Ph-H), 7.12 (t, J = 7.4 Hz, 4H, Ph-H), 7.15-7.30 (m, 40H, Ph-H), 7.56 (m, 8H, Ph-H). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ (ppm) -11.79 (t, ${}^{3}J_{PP} = ~13$ Hz, 4P, free *P*Ph₂), 40.73 (t, ${}^{2}J_{PP} + {}^{3}J_{PP}| = 24$ Hz, 2P, bound *P*_QPh₂), 49.54 (m, 2P, bridgehead *P*_M). ${}^{13}C{}^{1}H$ NMR (100 MHz, CDCl₃): δ (ppm) 20.37-22.55 (m, CH₂), 127.44-136.80 (Ph). UV-vis (CH₂Cl₂): $\lambda_{max}/mm (\varepsilon/M^{-1} \text{ cm}^{-1})$ 255sh (62078) 305sh (3825). MS ES+: *m*/*z* 1513 ([M+H]⁺ Calc.: 1513). (Found: C, 66.75; H, 5.66. Calc. for C₈₄H₈₄Cl₂P₈Ru: C, 66.67; H, 5.59%).

2.3.2 Trans-RuCl₂(PP[P=O]₂)₂(1b)

Hydrogen peroxide (0.15 mL, 30 wt. % in H₂O) was added to a solution of **1a** (0.027 g, 0.02 mmol) in CHCl₃ (5 mL). After stirring at room temperature in air for 75 min, the mixture was filtered through a plug of alumina grade II, eluting with additional CHCl₃. Solvent was removed *in vacuo* and the solid recrystallized from CH₂Cl₂/*n*-hexane to provide **1b** as a yellow solid (0.021 g, 72%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 1.79 (br m, 4H, CH₂), 2.01 (br m, 12H, CH₂), 2.24 (br m, 4H, CH₂), 2.69 (br m, 4H, CH₂), 6.74 (m, 8H, Ph–H), 6.81 (m, 4H, Ph–H), 7.31-7.69 (m, 48H, Ph–H). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ (ppm) 33.00 (t, 4P, ³J_{pp} = 17 Hz, *P*=O), 42.50 (t, 2P, $|^2J_{PP} + {}^3J_{PP}| = 22$ Hz, bound P_QPh_2), 52.57 (m, 2P, bridgehead $P_{\rm M}$). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ (ppm) 17.68-24.43 (m, CH₂), 127.53-135.91 (Ph). MS ES+: *m*/z 1577.2754 ([M+H]⁺ Calc. for C₈₄H₈₅Cl₂O₄P₈Ru: 1577.2769). (Found: C, 63.88; H, 5.26. Calc. for C₈₄H₈₄Cl₂O₄P₈Ru: C, 63.96; H, 5.37%).

<u>2.3.3 [(PP₃)Ru(η^3 -FcC₃CHFc)]PF₆(**2**)</u>

Triethylamine (0.12 mL, 0.86 mmol) was added to a mixture of RuCl₂(PP₃) (0.088 g, 0.10 mmol), ethynylferrocene (0.090 g, 0.43 mmol), and NaPF₆ (0.071 g, 0.42 mmol) in CH₂Cl₂ (8.5 mL). After stirring for 20 h in the absence of light, the cherry-red solution was filtered through a short Celite plug. Removal of solvent provided a dark red solid, which was eluted through a CH₂Cl₂ packed SiO₂ column using CH₂Cl₂-ethyl acetate (1:0 \rightarrow 6:4 v/v). Selected fractions from the second half of the primary orange band yielded 2 (~95% purity by ¹H NMR) as a dark red solid (0.028 g, 20%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 1.63 (br m, 2H, CH₂), 2.51 (br m, 4H, CH₂), 2.85 (br m, 2H, CH₂), 3.07 (br m, 2H, CH₂), 3.24 (br m, 2H, CH₂), 3.90 (br s, 5H, C₅H₅), 4.01-4.37 (br m, 4H, C₅H₄), 4.46 (s, 5H, C₅H₅), 4.74 (pseudo-t, 2H, C₅H₄), 5.01 (pseudo-t, 2H, C₅H₄), 5.56 (br s, 1H, C=CH), 6.7-7.2 (m, 30H, Ph-H). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ (ppm) -144.29 (sept, J_{P-F} = 713 Hz, 1P, PF_6), 42.90 (m, 2P, P_M), 70.59 (m, 1P, P_Q), 150.78 (m, 1P, P_A). ¹⁹F NMR (376.56 MHz, CDCl₃): -72.66 (d, $J_{F-P} = 715$ Hz, PF_6). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 28.16-29.16 (m, CH₂), 31.84-32.17 (m, CH₂), 66.80-72.69 (m, Cp), 70.35 (2C, Cp, CH), 70.55 (5C, Cp, CH), 72.56 (2C, Cp, CH), 128.04-138.84 (Ph). MS ES+: m/z 1336.1340 ([M]⁺ Calc. for $C_{66}H_{61}F_6Fe_2P_5Ru$: 1336.1108), 1191.1299 ([M-PF₆]⁺ Calc. for $C_{66}H_{61}Fe_{2}P_{4}Ru$: 1191.1466), 595.5543 ([M-PF₆]²⁺ Calc. for C₆₆H₆₁Fe₂P₄Ru: 595.5733). (Found: C, 63.88; H, 5.26. Calc. for C₆₆H₆₁F₆Fe₂P₅Ru: C, 59.34; H, 4.60%).

3. RESULTS AND DISCUSSION

3.1 Synthesis

Our interest in ruthenium complexes comprising the PP₃ ligand was sparked by the possibility of forcing octahedral dichlorides of the form RuX_2P_4 (X = halide, P = phosphine) into a *cis* geometry. Such materials are known to undergo rapid substitution to form the corresponding σ -alkynyl species,[13,16] which are of substantial current interest as conducting materials.[17-21] Following Bianchini *et al.*,[14] our initial attempts to prepare *cis*-RuCl₂(PP₃) from RuCl₂(PPh₃)₃ and 1.1 eq. PP₃ provided the expected material plus an additional, unexpected side product which was isolated following addition of EtOH to the product mixture in toluene. The latter was ultimately identified as RuCl₂(PP₃)₂ (**1a**), and could be prepared as the sole product under the same conditions by using 2 eq. PP₃. Attempts to prepare the iron and osmium congeners using conditions analogous to those used to synthesize their mono-ligated complexes (for example, heating 2 eq. PP₃ with OsCl₂(PPh₃)₃/FeCl₂ at reflux in 2-methoxyethanol/ethanol, respectively),[22,23] proved unsuccessful, producing only multiple product mixtures with no clear evidence for MCl₃(PP₃)₂.

Noting that pendant -PPh2 moieties in related complexes had been shown amenable to further modification,[24] we reacted 1a with an excess of hydrogen peroxide and observed that it readily forms an analogous complex with pendant -P(O)Ph₂ arms (1b, Scheme 1). In contrast, attempts to substitute the chloride groups, forming vinylidene or σ -alkynyl complexes, by reacting 1a in CH2Cl2 with ethynylbenzene/ethynylferrocene under 'Dixneuf' conditions (NaPF₆ followed by filtration through an alumina plug, or NaPF₆ and Et₃N together)[16,25,26] did not yield the desired products in appreciable yields. Under similar conditions we found that cis-RuCl₂(PP₃) (bright yellow) reacts with ethynylferrocene to provide the tri(hetero)metallic complex 2 (dark red; Scheme 1). This butenynyl complex is analogous to a family of previously reported materials – $[(PP_3)M(\eta^3 - RC_3CHR)]BF_4$ (M = Ru, Os; R = Ph, SiMe₃) – normally isolated as a mixture of isomers, and prepared from MH₂(PP₃).[27-29]

3.2 Spectroscopy

The ³¹P{¹H} NMR spectra of complexes **1a**, **1b** and **2** are particularly interesting (see Figure 2 and 3 for labeling scheme and representative spectra, respectively). In 1a, three resonances are observed with relative intensities 1:1:2 and a rather complicated splitting pattern. We consider that the pendant -PPh₂ moieties of each ligand are chemically non-equivalent (PA/B) as they cannot be interchanged by any symmetry operation (point group = C_i), and the bound $P_M/P_{M'}$ and $P_0/P_{O'}$ nuclei are magnetically non-equivalent as $J_{MQ} \neq J_{MQ'}$ (an ABMQ-ABM'Q' system). The resonance at δ 49.57 ppm can thus be attributed to the apical phosphorus atoms, PM (PM), appearing as a broad multiplet (unresolved dddd) due to ${}^{2}J$ coupling with $P_{Q'}(P_Q)$ and ³J coupling with P_A , P_B and $P_Q(P_Q)$. Further upfield at δ 40.70 ppm appears a pseudo-triplet (unresolved dd) assigned to the coordinated $-PPh_2$ group, P_0/P_0 , coupling to P_M and P_M . Finally, at δ -11.83 ppm there is another resonance, corresponding to the uncoordinated phosphorus atoms, P_A and P_B. As these have similar but non-identical chemical shifts (also notably comparable to that of -PPh₂ in the free ligand, at approximately δ –13 ppm), their overlapping doublets (from ${}^{3}J$ coupling to P_{M}/P_{M}) appear as a triplet. It was not possible to run homonuclear (${}^{31}P{}^{31}P{}$) decoupling NMR experiments with available spectrometers, but these could be used to verify our explanation of the observed spectral characteristics. The spectrum of 1b is similar to that of 1a, with the notable exception that the resonance attributable to PA/B environments have been shifted downfield by ~45 ppm due to oxidation (other environments exhibit downfield shifts a factor of ten smaller). A comparison of IR spectra for complexes 1a and **1b** (SI, Figure S13) suggest that an absorption at 2212 cm⁻¹ and two sets of overlapping peaks with maxima at 1170 and 1119 cm⁻¹ may be attributable to the P=O functionality (not being present in the spectrum of **1a**).

The ³¹P{¹H} NMR spectrum of complex **2** shows three well separated yet somewhat broadened resonances (certainly in comparison to the spectrum of RuCl₂[PP₃]), having relative intensities 1:1:2 (an AMQ₂ splitting pattern, typical of analogous octahedral Ru materials[14]). Though the splitting of each resonance cannot be clearly observed, it is straightforward from related studies to assign the resonance at 150.78 ppm to P_A (unresolved doublet of triplets), and those at 70.59 and 42.90 ppm to P_M (unresolved triplet of doublets) and P_Q (unresolved doublet of doublets), respectively. The single PF₆ counterion is also represented by a septet at –144.29 ppm with relative intensity 1.

Whilst the ¹H NMR spectra of **1a** and **1b** are straightforward (SI, Figures S1 and S3), that of 2 (SI, Figure S7) warrants further discussion. Two separate sets of ferrocenyl resonances are observed, and - along with a peak assigned to the vinylic proton at 5.56 ppm - appear broadened (with the upfield shifted ferrocenyl set extremely so). At present, the origin of broadening for these features remains uncertain. Attempts to sharpen the features using heteronuclear $({}^{1}H{}^{31}P{})$ decoupling experiments proved unsuccessful, although this did import additional detail to the CH₂ peaks (SI, Figure S10). At elevated temperature (328 K; SI, Figure S11) most resonances appear slightly sharpened, whereas various peaks become broader at low temperature (213 K; SI, Figure S12). It is possible that the broadened features at room temperature could result from local paramagnetic effects, for example if one of the ferrocene centres had been oxidized to Fe³⁺. However, only one PF_6^- counter ion is observed in the $^{31}P\{^1H\}$ NMR spectrum, and no readily assignable peaks above [M]⁺ were observed in mass spectra.

The stereochemistry of the butenynyl ligand was assigned based on NOESY experiments at 213 K which exhibited cross-peaks between the vinylic proton and a CH₂ resonance. Additional cross-peaks were observed between the substituted ring Cp-H (sharper set) and Ph-H resonances. As the vinylic proton appears directed towards the PP₃ ligand backbone (requiring the other substituent at that carbon to be directed away from the PP₃ backbone), and given that no cross-peaks were observed between the substituted Cp ring Cp-H (broader set) and Ph-H resonances, we suggest the extremely broadened set of ferrocenyl resonances are associated with the ferrocenyl group bound at the vinylic alkene. Assignment of the relative orientation of the butenynyl ligand with respect to the PP₃ ligand (vinylic alkene trans to P_A or P_M) was not attempted. Most ¹³C{¹H} resonances were also not easily individually assigned as a result of the low solubility of complexes, multiple overlapping environments and ¹³C-³¹P coupling for peaks associated with the PP3 ligand. Ranges for different nuclei environments are provided in the experimental section, with all observed peak values detailed in the SI (Figures S2, S5, and S8).



Figure 2. Labeling schemes used in ${}^{31}P{}^{1}H$ NMR assignments.





Figure 3. ${}^{31}P{}^{1}H$ NMR spectra of (a) 1a, (b) 1b and (c) 2 in CDCl₃.

3.3 Electrochemistry

All materials were studied by solution voltammetry in CH₂Cl₂/0.1 M NBu₄PF₆, and exhibited reversible behaviour under the described conditions $(i_{pa}/i_{pc} \sim 1, i_p \propto V_s^{1/2};$ data summarized in Table 1 and 2). Both 1a and 1b show only a single redox wave within the observable potential window, assigned to the Ru^{2+}/Ru^{3+} couple. It is apparent that oxidation of the pendant PPh₂ groups to P(=O)Ph₂ makes the Ru centre of 1b harder to oxidize than that of 1a by ~0.1 V. These values are similar to equilibrium potentials measured for analogous species such as trans-RuCl₂(dppe)₂,[30] (0.04 V vs. FcH/[FcH]⁺). The multi-nuclear complex 2, demonstrates two redox waves which are reversible if the potential range is set appropriately (Figure 4a). Extension to higher oxidation potentials reveals an additional, irreversible redox wave which also negatively impacts the reversible events previously observed (Figure 4b).

Table 1. Equilibrium potentials $(E_{1/2})$ and the difference in equilibrium potentials $(\Delta E_{1/2})$ for complexes **1a**, **1b** and **2**.^{*a*}

compound	$E_{1/2}^{\rm Fe1}$	$E_{1/2}^{\rm Fe2}$	$\Delta E_{1/2}$	$E_{1/2}^{Ru}$
$\operatorname{RuCl}_2(\operatorname{PP'}_3)_2(\mathbf{1a})$	-	-	-	0.116
RuCl ₂ (PP'P" ₂) ₂ (1b)	-	-	-	0.221
$[(PP_3)Ru(\eta^3 - FcC_3CHFc)]PF_6(2)$	-0.057	0.275	0.332	-

^{*a*} Scan rate 0.1 V s⁻¹. All potentials in V, reported relative to $[Cp_2Fe]^+/[Cp_2Fe]$. Measured with internal Cp_2^*Fe (-0.495 V vs. $Cp_2Fe/[Cp_2Fe]^+$).

 Table 2. Additional electrochemical data for complexes 1a, 1b

 and 2.^a

compound	redox transition	$E_{ m pa}$	$E_{\rm pc}$	ΔE	$i_{ m pa}/i_{ m pc}$
RuCl ₂ (PP' ₃) ₂ (1a)	$0 \rightarrow 1^+$	0.152	0.080	0.072	1.10
RuCl ₂ (PP'P" ₂) ₂ (1b)	$0 \rightarrow 1^+$	0.254	0.189	0.065	1.03
$[(PP_3)Ru(\eta^3 - FcC_3CHFc)]PF_6$ (2)	$0 \rightarrow 1^{+}$ $1^{+} \rightarrow 2^{+}$ $2^{+} \rightarrow 4^{+}$	-0.023 0.308 0.961^{b}	-0.092 0.242	0.069 0.066	1.05 0.91

^{*a*} For conditions see Table 1. ^{*b*} Estimated E_{pa} value obtained at a scan rate of 1 V s⁻¹, corrected for R_u .

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Figure 4. Cyclic voltammograms of **2** (V vs. FcH/[FcH]⁺, corrected for R_u). (a) Reversible 1e⁻ waves attributed to separated Fe²⁺/Fe³⁺ transitions (scan rate = 0.1 v s⁻¹). (b) Extension of potential window results in an irreversible process, attributed to Ru²⁺/Ru⁴⁺. Voltammograms shown are cycles 1 (solid blue curves), cycles 2, 5, 10 (dotted black curves) and 50 (solid red curves) (scan rate = 1 V s⁻¹).

We subjected a voltammogram of 2 comprising all three redox waves to further analysis (measured at 1 V s⁻¹; Figure 4b). For Nernstian waves, the difference between E_{pa} and $E_{pa/2}$ (the potential at $i_{pa/2}$) is 56.5/n mV at 25°C (where n is the stoichiometric number of electrons involved in the electrode process).[31] During our first cycle of measurement, successive oxidation waves exhibited i_{pa} ($E_{pa/2}$) values of 30.9 (-0.078), 27.0 (0.255) and 100.0 (0.922) μ A (V), respectively. Taking these values and data from Table 2, we find $|E_{pa} - E_{pa/2}|$ for each wave as 55, 53, and 39 mV. Taken together (and accounting for difficulties associated with defining the baseline for each wave), this analysis suggests that the observed redox waves are sequential 2 x 1e- (reversible), and 1 x 2e⁻ (irreversible) processes.

In this context, it is notable that the 4+ state is accessible in analogous ruthenium complexes – typically observed as an irreversible $\text{Ru}^{3+}/\text{Ru}^{4+}$ process occurring >0.80 V positive of redox waves associated with $\text{Ru}^{2+}/\text{Ru}^{3+}$.[13,32] If $E_{1/2}$ for **1a** and **1b** are taken as a reference point for where $\text{Ru}^{2+}/\text{Ru}^{3+}$ might occur in **2** (average $E_{1/2} \approx 0.17$ V), $\text{Ru}^{3+}/\text{Ru}^{4+}$ might be expected at $E_{1/2} \ge 0.97$ V. This is remarkably close to the measured $E_{\rm pa}$ of the irreversible wave (≈ 0.96 V vs. FcH/[FcH]⁺). The high value likely reflects the difficulty in removing 2e⁻ from [**2**]²⁺. We thus tentatively assign the irreversible, 2e⁻ process to the Ru²⁺/Ru⁴⁺ couple, and the reversible 1e⁻ processes to Fe²⁺/Fe³⁺. It is of further note that the $\Delta E_{1/2}$ of 0.332 V measured for **2** is ~0.222 V larger than for Fc-C=C-HC=CH-Fc ($\Delta E_{1/2} \sim 0.11$ V).[33,34] The latter has a similar connectivity between each Fe²⁺ centre, but no association with a Ru centre.

Before applying a potential externally, the measured open circuit potential for an electrolyte solution containing **2** ranged between -0.288 and -0.224 V vs. Pt, where $E_{1/2}^{Fe1} = 0.055$ V vs. Pt. These values offer further support to the conclusion that both ferrocene centres exist in the reduced state prior to volt-ammetry measurements (and so also in NMR experiments). If one ferrocene centre was already oxidized, the measured open circuit potential would be expected between $E_{1/2}^{Fe1}$ and $E_{1/2}^{Fe2}$.

3.4 X-ray crystallography

The crystal structure of **1a** (Figure 5) shows the complex to possess two bidentate phosphine ligands with the octahedral coordination sphere completed by a pair of *trans* chlorides; as a result of the ruthenium atom being situated on a centre of symmetry, the RuP₄ plane is perfectly flat. The phosphine ligand binds using the central phosphorus atom P1 and one of the three $-CH_2CH_2PPh_2$ arms (that based on P4), the other two being non-coordinating. These latter P–CH₂–CH₂–P arms adopt *anti* conformations (torsion angles of 166.70(11) and 174.41(14)° for the P1-P7 and P1-P10 arms respectively) whilst the bound arm has the expected *gauche* conformation (torsion angle 58.12(17)°).



Figure 5. The crystal structure of the C_i -symmetric complex 1a.

4. CONCLUSION

We have demonstrated how a simple change in reagent stoichiometry can provide Ru complexes comprising PP₃ ligands with unusual coordination geometries. The reactivity of pendant PPh₂ moieties towards H_2O_2 demonstrates a synthetic route to novel, metal-bound mixed phosphine-phosphine oxide ligands, and in general a new strategy (using the Ru centre as a blocking group) for the preparation of any number of unusual mixed ligand motifs based on PP₃. Furthermore, solution voltammetry studies of complex 2 indicates that interaction between ferrocene centres across a butenynyl bridge may be accentuated when the latter is coordinated to $Ru(PP_3)$. Our work lays the foundation for additional investigations into both Ru-PP₃ based transition metal-lanthanide, and functionalized butenynyl complexes within catalysis and materials chemistry.

ASSOCIATED CONTENT

Supporting Information

NMR, IR spectra and additional crystallographic information. This material is available free of charge via the Internet at http://www.sciencedirect.com.

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The authors declare no competing financial interest.

ACKNOWLEDGMENT

The authors thank Phillip Miller and Andreas Phanopoulos (Imperial College London, UK) for useful discussions and Peter Haycock for conducting NMR experiments. M.S.I., T.A. and N.J.L thank the EPSRC and the Leverhulme Trust (RPG 2012-754) for funding.

DEDICATION

Dedicated to Professor, the Lord Lewis (Jack) – a true gentleman and a leading light in inorganic and organometallic chemistry.

KEYWORDS

Ferrocenes, phosphines, multi-metallic, butenynyl, electrochemistry

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<u>Highlights</u>

- RuCl₂(diphos)₂ family extended to include coordinatively unsaturated PP₃ ligands.
- Pendant PPh₂ moieties available for further synthetic modification.
- *cis*-RuCl₂(PP₃) can react with ethynylferrocene to form butenylnyl species.
- Characterization includes solution voltammetry studies and X-ray crystallography.