#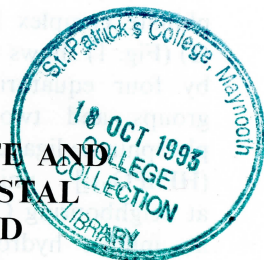 SYNTHESIS AND PROPERTIES OF TETRA-μ-ACETATODIRUTHENIUM(II,III) PHENYLPHOSPHINATE AND PHENYLPHOSPHONATE COMPLEXES: X-RAY CRYSTAL STRUCTURES OF [Ru$_2$(μ-O$_2$CCH$_3$)$_4$(HPhPO$_2$)$_2$]H AND [Ru$_2$(μ-O$_2$CCH$_3$)$_4$(PhPO$_3$H)$_2$]H · H$_2$O

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Abstract—Phenylphosphinic acid (HPhPO$_2$H) and phenylphosphonic acid (PhPO$_3$H$_2$) react with a methanolic solution of [Ru$_2$(μ-O$_2$CCH$_3$)$_4$(O$_2$CCH$_3$)$_2$]H · 0.7H$_2$O at room temperature to give [Ru$_2$(μ-O$_2$CCH$_3$)$_4$(HPhPO$_2$)$_2$]H (**1**) and [Ru$_2$(μ-O$_2$CCH$_3$)$_4$ (PhPO$_3$H)$_2$]H · H$_2$O (**2**), respectively. The X-ray crystal structures of **1** and **2** each show the Ru—Ru core to be ligated by four bridging bidentate acetate ligands [Ru—Ru distances: **1** = 2.272(1) Å; **2** = 2.267(2) Å] and two axial phenylphosphinate and phenylphosphonate ligands, respectively. In each complex the individual bimetallic molecules are linked together by a hydrogen ion which bridges the oxygen atoms of neighbouring axial ligands. In **2** the water molecule is also hydrogen-bonded to one of the axial phenylphosphonate groups. Spectroscopic, magnetic and cyclic voltammetric data for the complexes are given.

Phenylphosphinic acid (HPhPO$_2$H) and phenylphosphonic acid (PhPO$_3$H$_2$) are each renowned for their ability to form polymeric layered complexes with the *d*-block metals.[1–3] Recently,[4] we have shown that by employing pyridine as the reaction solvent monomeric copper(II) phenylphosphonate complexes can be prepared and the complexes [Cu(PhPO$_3$H)$_2$(C$_5$H$_5$N)$_4$] · 2CH$_3$OH and [Cu(PhPO$_3$H)$_2$(C$_5$H$_5$N)$_4$] were structurally characterized. Herein, we present details of the synthesis, structure and physical properties of the monomeric[5] tetra-μ-acetatodiruthenium(II,III) phenylphosphinate and phenylphosphonate complexes [Ru$_2$(μ-O$_2$CCH$_3$)$_4$(HPhPO$_2$)$_2$]H (**1**) and [Ru$_2$(μ-O$_2$CCH$_3$)$_4$(PhPO$_3$H)$_2$]H · H$_2$O (**2**), respectively.

Excess phenylphosphinic acid and phenylphosphonic acid each react at room temperature

with a methanolic solution of the diruthenium (II,III) complex [Ru$_2$(μ-O$_2$CCH$_3$)$_4$(O$_2$CCH$_3$)$_2$]H · 0.7H$_2$O[6–8] to give **1** and **2**, respectively. During both of these reactions the [Ru$_2$(μ-O$_2$CCH$_3$)$_4$]$^+$ moiety remains intact and the axial CH$_3$CO$_2^-$ ligands are replaced by HPhPO$_2^-$ and PhPO$_3$H$^-$.[9] The reaction of phenylphosphinic acid with [Ru$_2$(μ-O$_2$CCH$_3$)$_4$(O$_2$CCH$_3$)$_2$]H · 0.7H$_2$O contrasts with that found for the dicopper(II,II) complex [Cu$_2$(μ-O$_2$CCH$_3$)$_4$(H$_2$O)$_2$].[4] In the latter reaction the phenylphosphinic acid is oxidized to phenylphosphonic acid and is recovered as the monomeric copper(II) complex [Cu(PhPO$_3$H)$_2$(C$_5$H$_5$N)$_4$] · H$_2$O. This conversion of phenylphosphinic acid to the copper(II) phenylphosphonate complex was accompanied by the loss of the ν(P—H) IR stretching band. In the IR spectrum of **2** this medium intensity ν(P—H) band was present at 2370 cm^{-1}.

The X-ray crystal structure of the phenylphos-

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phinate complex $[Ru_2(\mu\text{-}O_2CCH_3)_4(HPhPO_2)_2]H$ (1) (Fig. 1) shows that the Ru—Ru core is ligated by four equatorial bridging bidentate acetate groups and two axial monodentate phenylphosphinate ligands. Individual $[Ru_2(\mu\text{-}O_2CCH_3)_4(HPhPO_2)_2]^-$ units in 1 are linked together at neighbouring O(6) atoms by a proton to give an infinite hydrogen-bonded chain. Thus, the complex is best formulated as $[Ru_2(\mu\text{-}O_2CCH_3)_4(HPhPO_2)_2]H$. This formulation is similar to that proposed[7] for the structurally characterized[8] starting complex $[Ru_2(\mu\text{-}O_2CCH_3)_4(O_2CCH_3)_2]H \cdot 0.7H_2O$.

The structure of the phenylphosphonate complex $[Ru_2(\mu\text{-}O_2CCH_3)_4(PhPO_3H)_2]H \cdot H_2O$ (2) (Fig. 2) is similar to that of the phenylphosphinate complex 1. Although the hydrogen-bonding hydrogen was not located directly in 2 the intermolecular distances between the oxygen atoms on neighbouring axial phenylphosphonate ligands [O(52)—O(62) = 2.431

Å] suggested that there was a proton bridging these two ligands. Hydrogen bonding was also present between the water molecule and one of the phenylphosphonate ligands. Thus, complex 2 is best formulated as $[Ru_2(\mu\text{-}O_2CCH_3)_4(PhPO_3H)_2]H \cdot H_2O$. It is interesting to note that in the structure of the phenylphosphinate complex 1 the phenyl groups are in the expected *trans* configuration with respect to each other, whereas in the phenylphosphonate complex 2 they are in the more sterically congested *cis* arrangement. It is thought that the latter stereochemistry may have been imposed, in part, by the more extensive hydrogen-bonding network that pervades 2.

The more important bond distances and angles for structures 1 and 2 are listed in Tables 1 and 2, respectively. The Ru—Ru and Ru—O(carboxylate) distances in each complex are similar to those reported for other Ru_2^{5+} complexes.[7,8,10–12] In addition, the Ru—O(phenylphosphinate or phenyl-
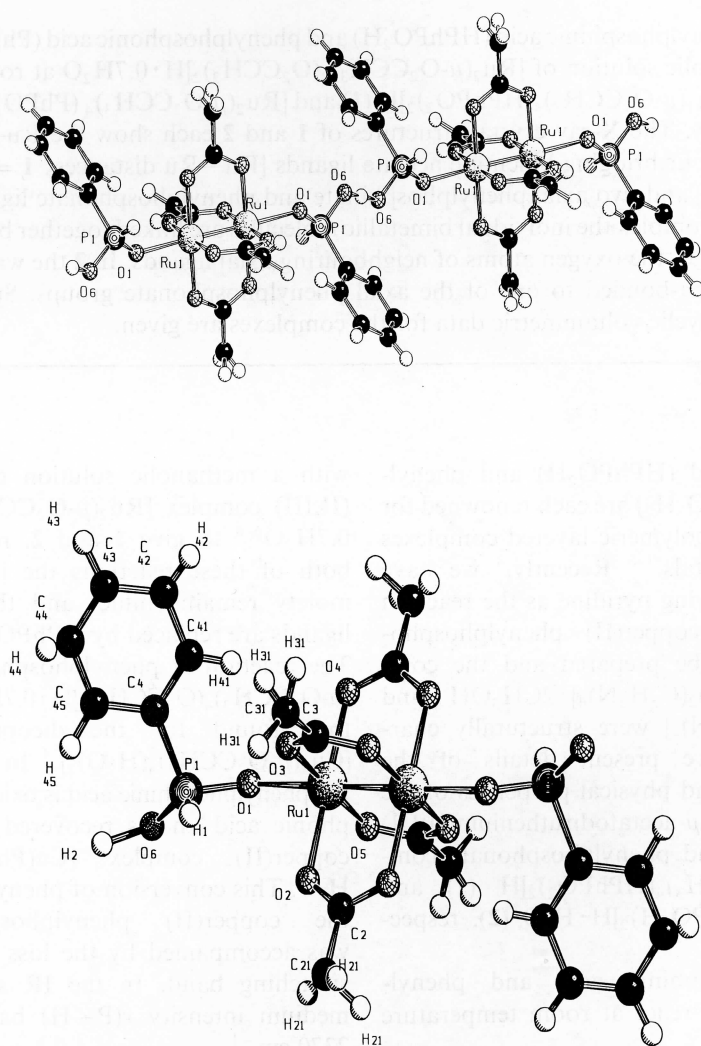

Fig. 1. X-ray crystal structure of $[Ru_2(\mu\text{-}O_2CCH_3)_4(HPhPO_2)_2]H$ (1).

Table 1. Selected bond lengths (Å) and angles (°) for **1**

Ru(1)—Ru(1)	2.272(1)		Ru(1)—O(1)	2.214(2)
Ru(1)—O(2)	2.026(2)		Ru(1)—O(3)	2.021(2)
Ru(1)—O(4)	2.026(2)		Ru(1)—O(5)	2.017(2)
P(1)—O(1)	1.495(2)		P(1)—O(6)	1.517(2)
P(1)—C(4)	1.791(3)		P(1)—H(1)	0.458(1)
O(6)—H(2)	1.202(2)			
O(2)—Ru(1)—O(1)	91.1(1)		O(3)—Ru(1)—O(1)	92.2(1)
O(3)—Ru(1)—O(2)	88.4(1)		O(4)—Ru(1)—O(1)	90.0(1)
O(4)—Ru(1)—O(2)	178.8(1)		O(4)—Ru(1)—O(3)	91.1(1)
O(5)—Ru(1)—O(1)	88.9(1)		O(5)—Ru(1)—O(2)	91.5(1)
O(5)—Ru(1)—O(3)	178.9(1)		O(5)—Ru(1)—O(4)	89.1(1)
O(6)—P(1)—O(1)	113.5(1)		P(1)—O(1)—Ru(1)	134.1(1)
H(2)—O(6)—P(1)	125.2(2)			
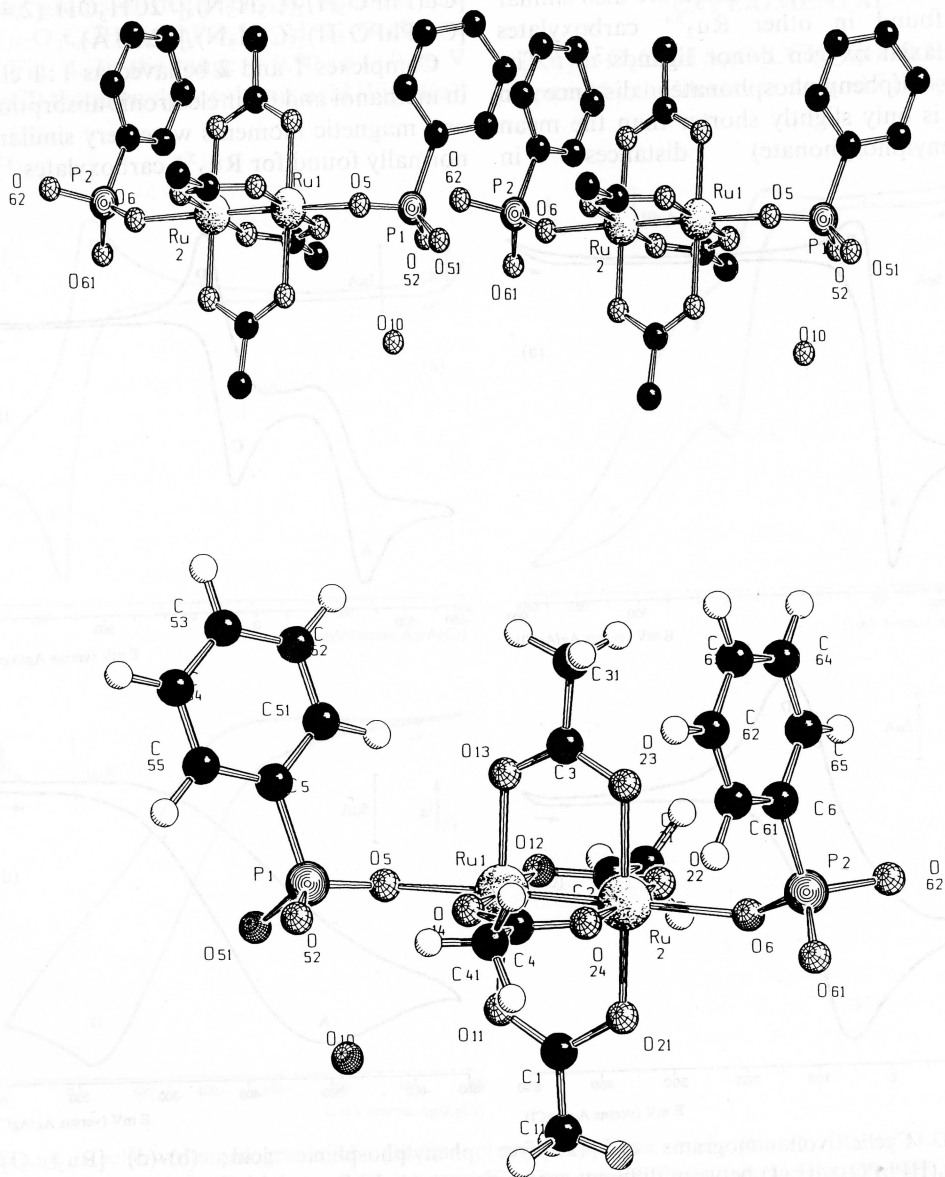
Fig. 2. X-ray crystal structure of [Ru$_2$(μ-O$_2$CCH$_3$)$_4$(PhPO$_3$H)$_2$]H·H$_2$O (**2**).

Table 2. Selected bond lengths (Å) and angles (°) for 2

Ru(1)—Ru(2)	2.267(2)		Ru(1)—O(11)	2.03(1)
Ru(1)—O(12)	2.03(1)		Ru(1)—O(13)	2.04(1)
Ru(1)—O(14)	1.99(1)		Ru(1)—O(5)	2.24(1)
Ru(2)—O(21)	1.99(1)		Ru(2)—O(22)	2.04(1)
Ru(2)—O(23)	2.02(1)		Ru(2)—O(24)	2.01(1)
Ru(2)—O(6)	2.22(1)		P(1)—O(5)	1.47(1)
P(1)—O(51)	1.54(1)		P(1)—O(52)	1.51(1)
P(2)—O(6)	1.48(2)		P(1)—C(5)	1.82(1)
P(2)—O(61)	1.57(1)		P(2)—O(62)	1.56(1)
P(2)—C(6)	1.80(1)		O(52)—O(62)	2.43(1)
O(5)—Ru(1)—Ru(2)	174.4(3)		O(5)—Ru(1)—O(12)	85.3(5)
O(5)—Ru(1)—O(14)	96.0(5)		O(6)—Ru(2)—Ru(1)	176.8(4)
O(6)—Ru(2)—O(22)	88.2(6)		O(6)—Ru(2)—O(24)	94.7(5)
P(1)—O(5)—Ru(1)	133.1(8)		P(2)—O(6)—Ru(2)	143.(1)

phosphonate) distances in **1** and **2** are also similar to those found in other Ru_2^{5+} carboxylates containing axial oxygen donor ligands.[7,8,12] The mean Ru—O(phenylphosphonate) distance in **2** (2.23 Å) is only slightly shorter than the mean Cu—O(phenylphosphonate) distances in

$[Cu(PhPO_3H)_2(C_5H_5N)_4]\cdot 2CH_3OH$ (2.42 Å) and $[Cu(PhPO_3H)_2(C_5H_5N)_4]$ (2.32 Å).[4]

Complexes **1** and **2** behaved as 1 : 1 electrolytes in methanol and their electronic absorption spectra and magnetic moments were very similar to those normally found for Ru_2^{5+} carboxylates.[13–15]
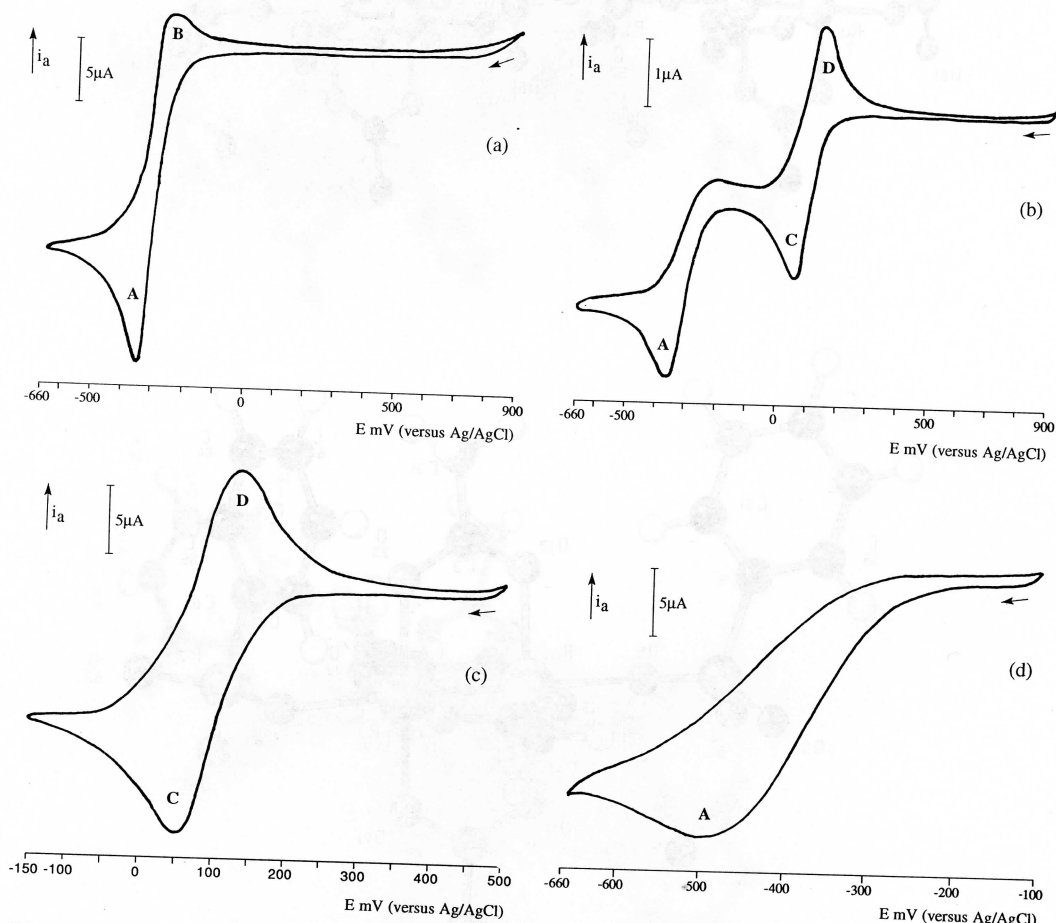

Fig. 3. Cyclic voltammograms of: (a) free phenylphosphinic acid; (b)–(d) [Ru₂(μ-O₂ CCH₃)₄(HPhPO₂)₂]H (**1**) between different switching potentials. Potentials are quoted with respect to the Ag/AgCl reference electrode. Scan rate = 20 mV s⁻¹.

Cyclic voltammograms of free phenylphosphinic acid and [Ru$_2$(μ-O$_2$CCH$_3$)$_4$(HPhPO$_2$)$_2$]H (**1**) are displayed in Fig. 3. In the potential range +0.90 to −0.66 V (vs Ag/AgCl) the free acid [Fig. 3(a)] showed a single quasi-reversible wave AB with $E_{1/2} = −298$ mV. Within the same potential limits complex **1** [Fig. 3(b)] showed a reversible wave (CD; $E_{1/2} = +100$ mV) for the Ru$_2$$^{5+}$/Ru$_2$$^{4+}$ couple[7,13] and an irreversible reduction wave (A; $E_c = −337$ mV), which is thought to be associated with the phenylphosphinate moieties. Figures 3(c) and 3(d) show the voltammograms of **1** recorded between the narrow potential ranges +0.50 to −0.15 V and −0.10 to −0.66 V, respectively, and these clearly demonstrate the reversibility of the Ru$_2$$^{5+}$/Ru$_2$$^{4+}$ couple and the irreversibility of the phenylphosphinate reduction.

Voltammograms of free phenylphosphonic acid and [Ru$_2$(μ-O$_2$CCH$_3$)$_4$(PhPO$_3$H)$_2$]H·H$_2$O (**2**) are shown in Fig. 4. In the range +0.90 to −0.66 V vs Ag/AgCl) the phenylphosphonic acid [Fig. 4(a)]

showed an essentially reversible redox couple (EF; $E_{1/2} = −369$ mV).[16] Across the same potential range complex **2** [Fig. 4(b)] exhibited an irreversible Ru$_2$$^{5+}$/Ru$_2$$^{4+}$ reduction (G; $E_c = +21$ mV) as well as a pair of broad ill-defined peaks (EF), which are thought to arise from the redox activity of the liberated phenylphosphonic acid. Figure 4(c) shows the voltammogram of **2** between the constricted potential limits of +0.30 to −0.05 V and this clearly illustrates the somewhat unusual irreversibility of the Ru$_2$$^{5+}$/Ru$_2$$^{4+}$ couple.

It is envisaged that **1** and **2** may be useful starting materials for the synthesis of polymeric phenylphosphinate and phenylphosphonate complexes containing strongly metal-to-metal bonded diruthenium centres.[9]

EXPERIMENTAL

[Ru$_2$(μ-O$_2$CCH$_3$)$_4$(O$_2$CCH$_3$)$_2$]H·0.7H$_2$O was prepared by the literature method.[8] IR spectra (KBr
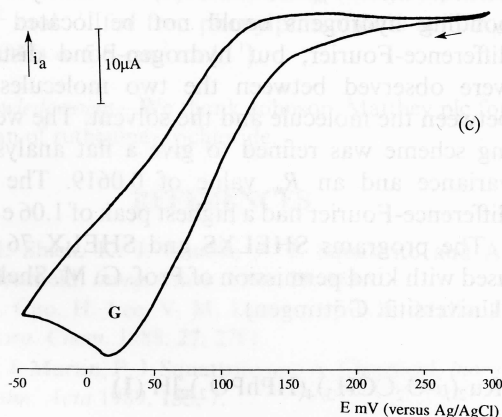
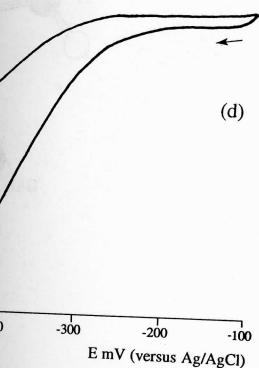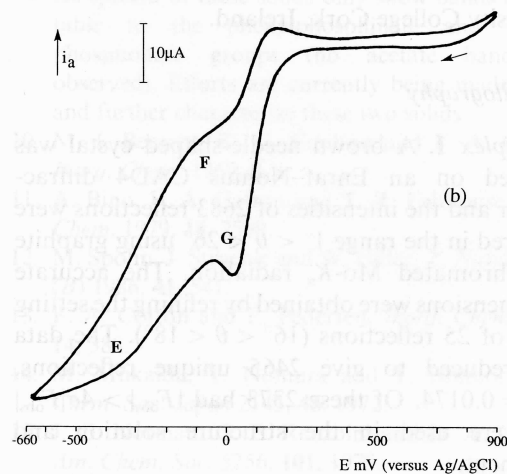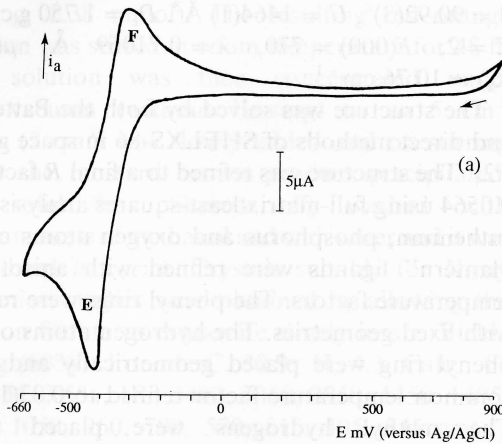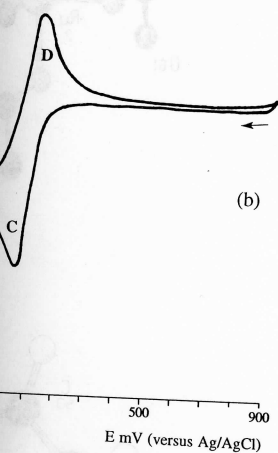Fig. 4. Cyclic voltammograms of: (a) free phenylphosphonic acid; (b), (c) [Ru$_2$(μ-O$_2$CCH$_3$)$_4$(PhPO$_3$H)$_2$]H·H$_2$O (**2**) between different switching potentials. Potentials are quoted with respect to the Ag/AgCl reference electrode. Scan rate = 20 mV s^{-1}.

discs) were recorded in the region 4000–200 cm^{-1} on a Perkin–Elmer 783 grating spectrometer and UV–vis spectra were obtained using a Milton Roy Spectronic 3000 Array. Room-temperature magnetic susceptibility measurements were made on a Johnson–Matthey Magnetic Susceptibility balance. An AGB Scientific Model 10 Conductivity meter was used for conductivity measurements. Cyclic voltammograms were recorded (*ca* 20°C and under nitrogen) using an EG&G Model 264A polarographic analyser and the data were analysed using the EG&G Condecon software package. A platinum bead and a platinum wire were used as the working and counter-electrodes, respectively. Tetra-n-butylammonium perchlorate in methanol (0.1 M) was used as the supporting electrolyte/solvent system. Sample concentration was 4.0×10^{-3} M and the scan rate was 20 mV s^{-1}. Potentials were recorded with respect to a silver–silver chloride reference electrode (3.5 M aqueous KCl), against which the ferrocene/ferrocenium(1+) couple had $E_{1/2} = +514$ mV. Elemental analyses were performed by the Microanalytical Laboratory, University College Cork, Ireland.

Crystallography

Complex 1. A brown needle-shaped cystal was mounted on an Enraf–Nonius CAD4 diffractometer and the intensities of 2683 reflections were measured in the range $1° < \theta < 26°$ using graphite monochromated Mo-K_α radiation. The accurate cell dimensions were obtained by refining the setting angles of 25 reflections ($16° < \theta < 18°$). The data were reduced to give 2465 unique reflections, $R_{merg} = 0.0174$. Of these 2373 had $|F_{obs}| > 4\sigma|F_{obs}|$ and were used in the structure solution and refinement.

Crystal data for C$_{20}$H$_{25}$O$_{12}$P$_2$Ru$_2$ (1), $M_r = 721.496$. Triclinic, P-1 (No. 2), $a = 7.585(2)$, $b = 8.002(2)$, $c = 12.413(3)$ Å, $\alpha = 99.76(1)$, $\beta = 93.69(1)$, $\gamma = 117.29(1)°$, $U = 652.7(3)$ Å^3, $D_c = 1.835$ g cm^{-3}, $Z = 1$, $F(000) = 358$, $\lambda = 0.71069$ Å, μ(Mo-K_α) = 12.00 cm^{-1}.

The structure was solved using the Patterson method of SHELXS-86 with some operator intervention and was found to have half a molecule in the asymmetric unit. The rutheniums were found to have bridging acetate groups and the phenylphosphinate ligands in the axial positions. The structure was refined by full-matrix least-squares with all the non-hydrogen atoms anisotropic. The hydrogen atoms were located from difference-Fourier and allowed to refine with the exception of the bridging hydrogen, which is disordered and the hydrogen attached to the phosphorus. These hydro-

gens were located but were not allowed to refine. The refinement was weighted to give a flat analysis of variance and a final R of 0.0344 and R_w of 0.0373. The difference-Fourier had a highest peak of 1.2 e Å^{-1} in the vicinity of the ruthenium atom.

Complex 2. A small brown crystal was mounted on the above-mentioned diffractometer. The cell parameters were determined by refining the setting angles of 25 reflections with $14° < \theta < 16°$. The intensities of 3797 reflections ($\pm h$, $\pm k$, $+l$) in the range $1° < \theta < 22°$ were measured using graphite monochromated Mo-K_α radiation. The Laue symmetry of the diffraction pattern was not clear (although the lattice geometry was very close to orthorhombic) so the data were collected in triclinic symmetry. The structure was solved satisfactorily in the space group $P2_1$. The data were merged to give the unique non-centrosymmetric quadrant of data—1908 unique reflections (merging $R = 0.1144$), of which 1695 had $F_{obs} > 4\sigma F_{obs}$ and were used for structure solution and refinement.

Crystal data for C$_{20}$H$_{27}$O$_{15}$P$_2$Ru$_2$ (2), $M_r = 771.509$. Monoclinic, $P2_1$ (No. 4), $a = 11.361(4)$, $b = 11.040(5)$, $c = 11.679(6)$ Å, $\beta = 90.92(3)°$, $U = 1464(1)$ Å^3, $D_c = 1.750$ g cm^{-3}, $Z = 2$, $F(000) = 770$, $\lambda = 0.71069$ Å, μ(Mo-K_α) = 10.76 cm^{-1}.

The structure was solved by both the Patterson and direct methods of SHELXS-86 in space group $P2_1$. The structure was refined to a final R factor of 0.0564 using full-matrix least-squares analysis. The ruthenium, phosphorus and oxygen atoms of the "lantern" ligands were refined with anisotropic temperature factors. The phenyl rings were refined with fixed geometries. The hydrogen atoms on the phenyl ring were placed geometrically and their common temperature factor refined to 0.03(1) Å^2. The methyl hydrogens were placed using SHELX76, but not refined, and their common temperature factor refined to 0.18(6) Å^2. The hydrogenbonding hydrogens could not be located from difference-Fourier, but hydrogen-bond distances were observed between the two molecules and between the molecule and the solvent. The weighting scheme was refined to give a flat analysis of variance and an R_w value of 0.0619. The final difference-Fourier had a highest peak of 1.06 e Å^{-1}.

The programs SHELXS and SHELX 76 were used with kind permission of Prof. G. M. Sheldrick (Universität Göttingen).

[Ru$_2$(μ-O$_2$CCH$_3$)$_4$(HPhPO$_2$)$_2$]H (1)

To a solution of [Ru$_2$(μ-O$_2$CCH$_3$)$_4$(O$_2$CCH$_3$)$_2$]H · 0.7H$_2$O (0.30 g, 0.52 mmol) in methanol (60 cm^3) under nitrogen was added phenylphosphinic acid

(0.77 g, 5.42 mmol). The resulting red–brown solution was stirred at room temperature for 48 h. The solution was then concentrated under high vacuum (without heating) until the mustard–brown product precipitated. The solid was filtered off, washed with small amounts of methanol and with water and it was then dried *in vacuo*. Crystals suitable for X-ray diffraction studies were obtained by allowing the reaction filtrate to evaporate slowly in air. Yield: 0.26 g (69%). Found: C, 33.5; H, 3.3. Calc.: C, 33.3; H, 3.5%. IR: 3440, 3050, 2940, 2370, 1590, 1440, 1400, 1360, 1140, 1050, 1000, 970, 750, 690, 530, 400, 340 cm^{-1}; $\mu = 3.97$ B.M. per Ru₂ unit; λ_{max} (CH₃OH) $= 429$ nm ($\varepsilon = 712$ mol^{-1} dm^3 cm^{-1}); Λ_M (CH₃OH) $= 49$ S cm^2 mol^{-1} [for free phenylphosphinic acid Λ_M (CH₃OH) $= 15$ S cm^2 mol^{-1}].

[Ru₂(μ-O₂CCH₃)₄(PhPO₃H)₂]H·H₂O (2)

To a solution of [Ru₂(μ-O₂CCH₃)₄(O₂CCH₃)₂]H·0.7H₂O (0.30 g, 0.52 mmol) in methanol (60 cm^3) under nitrogen was added phenylphosphonic acid (0.85 g, 5.38 mmol). The resulting red–orange solution was stirred at room temperature for 48 h. The solution was then concentrated under high vacuum (without heating) to *ca* 5 cm^3. Water (2 cm^3) was slowly added and on stirring in air the mustard–brown product precipitated. The solid was filtered off, washed with small amounts of methanol and with water and it was then dried *in vacuo*. Crystals suitable for X-ray diffraction studies were obtained by allowing the reaction filtrate to evaporate slowly in air. Yield: 0.24 g (60%). Found: C, 30.9; H, 4.3. Calc.: C, 31.1; H, 3.5%. IR: 3460, 3060, 2950, 1450, 1405, 1150, 1050, 960, 700, 570, 515, 405, 345 cm^{-1}; $\mu = 3.97$ B.M. per Ru₂ unit; λ_{max} (CH₃OH) $= 428$ nm ($\varepsilon = 765$ mol^{-1} dm^3 cm^{-1}); Λ_M (CH₃OH) $= 53$ S cm^2 mol^{-1} [for free phenylphosphonic acid Λ_M (CH₃OH) $= 5$ S cm^2 mol^{-1}].

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5. Although complexes **1** and **2** are essentially polymeric in the solid state by virtue of the intermolecular hydrogen bonding at the axial ligands we wish to distinguish them from those polymeric solids in which each phenylphosphinate and phenylphosphonate ligand uses two of their oxygen atoms to bridge adjacent metal centres (see refs 1–3). Thus, in terms of the monodentate coordination of the phenylphosphinate and phenylphosphonate ligands in **1** and **2** these complexes are best described as being monomeric.
6. [Ru₂(μ-O₂CCH₃)₄(O₂CCH₃)₂]H·0.7H₂O (see ref. 7) was originally incorrectly formulated as [Ru₂(μ-O₂CCH₃)₄(O₂CCH₃)₂]·H₂O (see ref. 8).
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9. When excess phenylphosphinic acid and phenylphosphonic acid are each reacted with [Ru₂(μ-O₂CCH₃)₄(O₂CCH₃)₂]H·0.7H₂O in refluxing methanol paramagnetic brown solids are obtained. The IR spectra of these solids only show bands attributable to the phenylphosphinate and phenylphosphonate groups (no acetate bands are observed). Efforts are currently being made to try and further characterize these two solids.
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16. We have found (see ref. 4) that in the potential region +0.80 to −1.70 V (vs Ag/AgCl) free phenylphosphonic acid was electroinactive in a 1:4 pyridine:methanol solution. It is likely that in this solvent mixture the pyridinium salt [C₅H₅NH]⁺[PhPO₃H]⁻ is formed and that the [PhPO₃H]⁻ ion is electroinactive. This suggests that in the voltammogram of **2** it is the free phenylphosphonic acid (and not the phenylphosphonate anion) that is liberated upon dissolving the complex in methanol that is giving rise to the broad waves EF in Fig. 4(b). In the same pyridine:methanol solvent mixture free phenylphosphinic acid has also been found to be electroinactive between +0.80 to −1.00 V. However, beyond −1.10 V a large irreversible reduction wave was observed for this acid.

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...n crystal was mounted ...ffractometer. The cell ...by refining the setting ...h $14° < \theta < 16°$. The ...s ($\pm h, \pm k, +l$) in the ...asured using graphite ...iation. The Laue sym...attern was not clear ...try was very close to ...re collected in triclinic ...s solved satisfactorily ...e data were merged to ...ymmetric quadrant of ...eflections (merging ...had $F_{obs} > 4\sigma F_{obs}$ and ...ion and refinement.

...$_{20}H_{27}O_{15}P_2Ru_2$ (2), ...$P2_1$ (No. 4), ...), $c = 11.679(6)$ Å, ...^{3}. $D_c = 1.750$ g cm^{-3}, ...0.71069 Å, μ(Mo-

...by both the Patterson ...XS-86 in space group ...d to a final R factor of ...-squares analysis. The ...oxygen atoms of the ...ned with anisotropic ...nyl rings were refined ...ydrogen atoms on the ...ometrically and their ...refined to 0.03(1) Å^2. ...were placed using ...d their common tem...(6) Å^2. The hydrogen-...not be located from ...ogen-bond distances ...two molecules and ...e solvent. The weight-...ive a flat analysis of ...of 0.0619. The final ...st peak of 1.06 e Å^{-1}. ...nd SHELX 76 were ...Prof. G. M. Sheldrick

...]H (1)

...CH₃)₄(O₂CCH₃)₂]H· ...n methanol (60 cm^3) ...henylphosphinic acid