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Synthesis, characterization and electrochemistry of cyclopentadienyl phosphine nitrosyl cyanide complexes of ruthenium(II) and osmium(II). Preparation of the dicyano ruthenium(II) complex, $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{CN})_2]\text{Na}$

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Abstract

A series of novel chiral metal centre complexes of the general form, $[\text{"cp"}\text{M}(\text{PPh}_3)(\text{NO})(\text{CN})]\text{PF}_6$ with "cp" = $\eta^5\text{-C}_5\text{H}_5$, M = Ru (1); "cp" = $\eta^5\text{-C}_5\text{H}_4\text{-Me}$, M = Ru (2); "cp" = $\eta^5\text{-C}_5\text{Me}_5$, M = Ru (3) and "cp" = $\eta^5\text{-C}_5\text{H}_5$, M = Os (4), has been synthesized in 85% yield from the corresponding *bis*-phosphine complexes, $[\text{"cp"}\text{M}(\text{PPh}_3)_2\text{CN}]$, and characterized by NMR (^1H ; ^{31}P ; ^{13}C) and FTIR spectroscopies. Cyclic voltammetry of 1–4 indicates quasi-reversible $\text{M}^{1/\text{II}}$ redox couples at potentials (*vs.* KCl(aq) SCE) of $E_{1/2}$ –0.125, –0.155, –0.30 and –0.315 V, respectively. Near quantitative syntheses of the precursor *bis*-phosphine cyanide complexes, from the *bis*-phosphine halides, have been achieved by using methanolic sodium cyanide. The complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{CN})_2]\text{Na}$ (6) has been synthesized by treating 1 with sodium azide in acetonitrile followed by methanolic sodium cyanide.

1. Introduction

Amongst the transition metals, ruthenium is believed to have the greatest affinity for the nitrosyl ligand [1]. Cationic cyclopentadienyl-ruthenium nitrosyls have been reported [2–4] but to our knowledge none contain the "cp"Ru(CN) fragment. The complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{NO})(\text{Cl})]\text{PF}_6$ (5) has recently been prepared by Simpson *et al.* from treatment of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ with sodium nitrite and refluxing ethanolic hydrochloric acid. The mechanism is believed to involve the sterically-assisted loss of one triphenylphosphine ligand. The acidic conditions serve to trap the liberated phosphine and to generate nitrous acid as a source of nitrosonium ions. In view of our interest in cyclopentadienyl-metal cyanides we decided to investigate an analogous reaction involving $[(\eta^5\text{-C}_6\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{CN}]$ (P1) in the hope of preparing $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{NO})(\text{CN})]\text{PF}_6$ (1) and investigating the synthetic possibilities of the electrophilic nitrosyl centre [12].

The previously reported preparations of P1 [5], from $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ in refluxing alcoholic potassium cyanide solutions for two hours, give moderate to high yields. We decided to modify this procedure by using the more soluble sodium cyanide in methanol in the hope of increasing the yield.

2. Results and discussion

2.1. Syntheses

When a mixture of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ and a five-fold excess of sodium cyanide in methanol is refluxed a bright yellow solution is formed within a few minutes. The reaction is most conveniently performed using a conventional microwave oven. Following extraction and recrystallization, pure crystals of the desired cyanide complex are obtained in near quantitative yield (> 95%). The set of *bis*-phosphine precursors P1–P4 was synthesized in the same way. In no instance was there evidence for the replacement of triphenylphosphine by cyanide to form dicyano complexes of the form $[\text{"cp"}\text{M}(\text{PPh}_3)(\text{CN})_2]^-$.

With minor modifications of the method reported by Simpson *et al.* [4], the novel cyclopentadienyl-metal

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TABLE 1. Analytical data for the cyclopentadienyl-metal complexes

Complex		Colour	Analysis Found (Calc.) %		
			C	H	N
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{CN}]^{\text{a}}$	P1	pale yellow	63.8(64.4)	4.8(4.7)	1.8(1.8)
$[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Ru}(\text{PPh}_3)_2\text{CN}]^{\text{b}}$	P2	pale yellow	66.3(66.2)	5.0(4.9)	1.9(1.8)
$[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PPh}_3)_2\text{CN}]$	P3	bright yellow	71.2(71.7)	5.8(5.8)	1.8(1.8)
$[(\eta^5\text{-C}_5\text{H}_5)\text{Os}(\text{PPh}_3)_2\text{CN}]$	P4	cream-white	62.6(62.6)	4.7(4.4)	1.8(1.7)
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{NO})(\text{CN})]\text{PF}_6$	1	orange	45.4(45.8)	3.2(3.2)	4.5(4.5)
$[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Ru}(\text{PPh}_3)(\text{NO})(\text{CN})]\text{PF}_6$	2	orange	46.3(46.7)	3.3(3.5)	4.3(4.4)
$[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PPh}_3)(\text{NO})(\text{CN})]\text{PF}_6$	3	orange	49.6(49.8)	4.4(4.3)	4.0(4.0)
$[(\eta^5\text{-C}_5\text{H}_5)\text{Os}(\text{PPh}_3)(\text{NO})(\text{CN})]\text{PF}_6$	4	lemon yellow	39.5(40.1)	2.8(2.8)	3.9(3.9)
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{CN})_2]\text{K}^{\text{c}}$	6	yellow-white	56.2(57.8)	4.1(3.9)	5.2(5.4)

^a With $1\text{CH}_2\text{Cl}_2$ of crystallization. ^b With $0.75\text{CH}_2\text{Cl}_2$ of crystallization. ¹H NMR δ 4.3 ppm for CH_2Cl_2 . ^c The potassium salt was prepared from the sodium salt by dissolution in methanol and subsequent addition of aqueous potassium iodide solution. FAB + mass spectrometry revealed principal cluster peaks $m^+/z = 520, 559$ associated with **6** and **6** + K^+ respectively.

nitrosyl cyanide complexes **1–4**, prepared from the precursor set **P1–P4**, were isolated in 85% yield.

Nitrosyls of ruthenium(II) are known to undergo attack by nucleophiles such as hydrazine, azide, and hydroxide ion [6,10,12]. A slight excess of methanolic sodium azide was therefore added to a solution of **1** (~ 15 mg) in dry acetonitrile and the reaction monitored by cyclic voltammetry and infrared spectroscopy. Within two hours the redox couple from **1** had com-

pletely disappeared. An infrared spectrum of a sample of the solution showed no metal-coordinated nitrosyl absorptions. We suggest that the product is $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{MeCN})\text{CN}]$ (**7**). Metal-acetonitrile complexes are known to be synthetically useful as a consequence of substitution by π -acid ligands [7,8]. We therefore investigated the reaction of **7** with refluxing methanolic sodium cyanide solution in an attempt to generate the novel complex ion $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)\text{-}$

TABLE 2. ^1H , ^{31}P and ^{13}C NMR data for the cyclopentadienyl-metal complexes ^a

	^1H NMR	^{31}P NMR	^{13}C NMR
P1	4.42(s, 5H, C_5H_5)	47.13	85.2(s, C_5), 127.6(s, Ph), 128.9(s, Ph), 133.6(s, Ph), 138.0(m, C_{ipso})
P2	4.13(s, 2H), 3.95(s, 2H), 1.93(s, 3H, CH_3)	47.64	13.0(s, $\text{C}-\text{CH}_3$), 83.6(s, C_4), 94.9(s, C_4), 102.7(s, $\text{C}-\text{CH}_3$) 127.5(s, Ph), 128.8(s, Ph), 133.7(s, Ph), 138.2(m, C_{ipso})
P3	1.21(s, 15H, CH_3)	49.61	9.7(s, $\text{C}-\text{CH}_3$), 94.1(s, C_5), 127.1(s, Ph), 128.5(s, Ph), 134.4(s, Ph), 136.5(m, Ph)
P4	4.40(s, 5H, C_5H_5)	-0.66	81.3(s, C_5), 127.4(s, Ph), 128.9(s, Ph), 133.6(s, Ph), 138.3(m, C_{ipso})
1	6.44(2, 5H, C_5H_5) ^b	35.21 ^b	101.5(s, C_5), 129.2(d, $J(\text{CP})$ 58.6, C_{ipso}), 130.6(d, $J(\text{CP})$ 11.7, C_{meta}), 134.0(s, C_{para}), 134.4(d, $J(\text{CP})$ 10.4, C_{ortho}) ^c
2	6.2(m, 1H), 5.90(m, 1H), 5.74(m, 1H), 5.65(m, 1H), 2.24(d, $J(\text{PH})$ 1.5, 3H, CH_3) ^c	35.43 ^b	14.0(s, $\text{C}-\text{CH}_3$), 98.0(s, C_4), 100.1(s, C_4), 10.7(s, C_4), 101.0(s, C_4), 125.0(s, $\text{C}-\text{CH}_3$), 129.3(d, $J(\text{CP})$ 58.3, C_{ipso}), 130.6(d, $J(\text{CP})$ 12.0, C_{meta}), 134.0(s, C_{para}), 134.3(d, $J(\text{CP})$ 9.7, C_{ortho}) ^c
3	1.69(d, $J(\text{PH})$ 2.2, 15H,	34.36	10.4(s, $\text{C}-\text{CH}_3$), 114.0(s, C_5), 128.5(d, $J(\text{CP})$ 53.9, C_{ipso}), 130.5(d, $J(\text{CP})$ 10.6, C_{meta}), 133.7(s, C_{para}), 134.5(d, $J(\text{CP})$ 10.3, C_{ortho}) ^c
4	6.57(s, 5H, C_5H_5) ^b	-5.40 ^b	98.0(s, C_5), 128.6(d, $J(\text{CP})$ 65.6, C_{ipso}), 130.6(d, $J(\text{CP})$ 12.2, C_{meta}), 134.3(s, C_{para}), 134.4(d, $J(\text{CP})$ 10.2, C_{ortho}) ^c
5 ^{b,c}	6.43(s, 5H, C_5H_5)	37.7	103.4(s, C_5), 129.3(d, $J(\text{CP})$ 57.5, C_{ipso}), 133.5(d, $J(\text{CP})$ 11.6, C_{meta}), 133.7(s, C_{para}), 134.5(d, $J(\text{CP})$ 10.6, C_{ortho})
6 ^d	4.55(s, 5H, C_5H_5)	58.25	82.8(s, C_5), 128.1(d, $J(\text{CP})$ 9.6, C_{meta}), 129.8(s, C_{para}), 134.6(d, $J(\text{CP})$ 10.2, C_{ortho}), 139.6(d, $J(\text{CP})$ 44.1, C_{ipso})

^a s singlet, d doublet, m multiplet. Chemical shifts quoted as δ (ppm) and coupling constants as J (Hz). Recorded in CDCl_3 unless stated otherwise. Complexes **1–4** display a weak septet in the region $\delta -30$ to -40 ppm of the ^{31}P spectrum, characteristic of the hexafluorophosphate anion; $J(\text{PF}) \sim 700$ Hz. The ^1H spectra of the complexes all display multiplets in the region $\delta 7.0$ – 7.8 ppm with the appropriate integrated intensities for the triphenylphosphine ligands. ^b Recorded in $(\text{CD}_3)_2\text{CO}$. ^c Reference [4]. ^d Recorded in CD_3OD . ^e Recorded in CD_3CN .

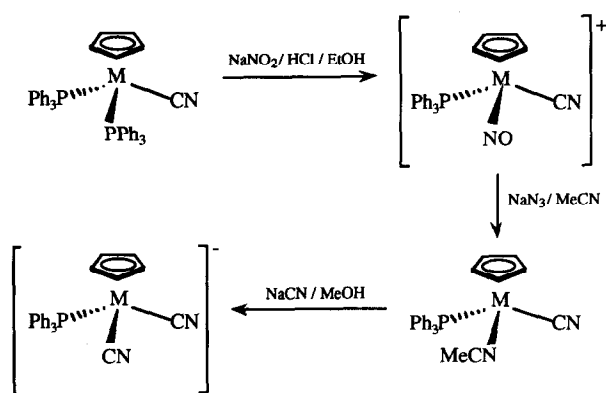


Fig. 1.

(CN)₂][−] (**6**). The identity of the product was confirmed as **6** by spectroscopic, mass spectrometric, and micro-analytical techniques (Tables 1–3).

The reaction scheme for these conversions is summarized in Figure 1.

2.2. Properties

The *bis*-phosphine cyanides **P1–P4** and the corresponding nitrosyl complexes **1–4** are air-stable solids. The nitrosyl complexes are most soluble in acetonitrile and acetone, and seem indefinitely stable in aerated solutions, whereas their precursors slowly decompose during several days. The dicyano complex, **6** is air-stable, very soluble in methanol, sparingly soluble in acetonitrile and acetone and slightly soluble in water. All solutions of **6** appear to be air-stable.

2.3. Spectroscopy

Characteristic NMR data for the complexes are shown in Table 2. The large downfield shift (~ 2 ppm) between, for example, **P1** and **1** reflects the cationic

nature of **1**, and more specifically the pronounced π -accepting ability of the nitrosyl ligand. Except for that of the monomethylcyclopentadienyl analogue, **2**, the ¹H NMR spectra of the nitrosyl complexes display a single cyclopentadienyl ring resonance. Compound **2** displays four noticeably broader resonances, with equal integrals, having a quartet-related structure in the corresponding region, whereas the precursor, **P2**, shows two sharp singlets. Rapid ring rotation in solution creates two inequivalent proton pairs in **P2**, whereas in **2** the introduction of a chiral metal centre removes this equivalence. The effect is also clearly seen in the ¹³C spectrum, with four peaks in the corresponding cyclopentadienyl-carbon region. The ¹H NMR spectrum of the monomethyl and pentamethyl nitrosyls **2** and **3** display a split resonance at δ 2.24 and 1.69 ppm, respectively; methyl protons are coupled to phosphorus: $J(\text{PH}) = 1.5$ and 2.2 Hz respectively.

The infrared spectra of both complex sets are shown in Table 3. The nitrosyls show new absorption peaks, relative to their precursors, in the regions 1840–1860, 2120–2140, 850 and 559 cm^{−1} which can be assigned to $\nu(\text{NO})$, $\nu(\text{CN})$, $\nu(\text{PF})$ and $\nu(\text{MN})$ vibrations respectively. The assignment of the latter is consistent with other nitrosyls of ruthenium(II) [6]. We note especially that, whilst the infrared region (400–1700 cm^{−1}) scarcely varies between **P1**, **1** and **6**, the peak at 559 cm^{−1} is unique to the nitrosyl. The $\nu(\text{NO})$ peaks are indicative and typical for linearly bound nitrosyls [11]. The increase in the cyanide frequency of about 65 cm^{−1} relative to that of the precursor cyanide, can be understood in terms of reduced metal π back-bonding to the cyanide due to the competitive π -acidity of the nitrosyl ligand. It is of interest to compare this trend with those for the related complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{CO})\text{CN}]$ [9], $\nu(\text{CO}) = 1980$, $\nu(\text{CN}) =$

TABLE 3. Electrochemical ^a and infrared ^b data for the cyclopentadienyl-metal complexes

	$E_{1/2}/\text{V}$	$E_{\text{p,a}}/\text{V}$	$E_{\text{p,c}}/\text{V}$	$\nu(\text{CN})/\text{cm}^{-1}$	$\nu(\text{NO})/\text{cm}^{-1}$	$\nu(\text{MN})/\text{cm}^{-1}$
P1	–	+0.88	–	2079	–	–
P2	–	+0.82	–	2072	–	–
P3	+0.57, +1.18 ^d	+0.60, +1.23	+0.53, +1.13	2066	–	–
P4	+0.77	+0.805	+0.725	2065	–	–
1	+0.125	−0.085	−0.165	2136	1865	558
2	−0.155	−0.115	−0.19	2132	1858	558
3	−0.30	−0.255	−0.34	2128	1836	558
4	−0.315	−0.33	−0.455	2138	1850	557
5	–	+0.15 ^e	−0.27 ^e	–	1849 ^c	–
6	–	+0.42	–	2041, 2062	–	–

^a Redox potentials are quoted for a scan rate of 100 mV s^{−1} and defined according to $E_{1/2} = 1/2(E_{\text{p,a}} + E_{\text{p,c}})$ where $E_{\text{p,a}}$ and $E_{\text{p,c}}$ refer to anodic(oxidative) and cathodic(reductive) peak potentials. Under the same conditions the redox potential for the standard ferrocene/ferrocinium couple (Fc/Fc⁺) was found to be +0.415 V. ^b As KBr pellets. ^c Reference [4]. ^d We assign the couples as reversible Ru^{II/III} and irreversible Ru^{III/IV} processes respectively. ^e We assign these irreversible half-couples respectively to a Ru^{II/I} reductive wave, $E_{\text{p,c}}$, in **5** and a Ru^{I/II} oxidative wave, $E_{\text{p,a}}$, in a solvated species, possible $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{NO})(\text{MeCN})]^+$ (Fig. 2).

2104, $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(\text{CN})_2]^-$ [9], $\nu(\text{CO}) = 1960$, $\nu(\text{CN}) = 2095$, 2110 cm^{-1} and $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{CN})_2]^-$, **6**, with cyanide peaks at 2041 and 2062 cm^{-1} . These frequency trends are consistent with the known π -accepting series, $\text{NO}^+ > \text{CO} > \text{PPh}_3 > \text{CN}^-$. In **1–3** the inductive effect of the ring methyl groups is small, and tends to lower the frequency of both $\nu(\text{NO})$ and $\nu(\text{CN})$ vibrations by facilitating metal π back-bonding.

2.4. Electrochemistry

Electrochemical data for precursor and nitrosyl complex sets are shown in Table 3. With a high scan rate ($\sim 200\text{ mV s}^{-1}$), complexes **P1** and **P2** display irreversible couples (only the oxidative half-couple peaks, $E_{\text{p,a}}$, are evident) whereas **P3** and the osmium analogue, **P4**, show quasi-reversible behaviour. At low scan rates ($\sim 10\text{ mV s}^{-1}$), only the anodic peak, $E_{\text{p,a}}$, is observed for the latter complex. We suggested that the rates of electron-transfer and electroactive product decomposition are competing in the redox process of **P4**. As reported elsewhere for analogous complexes [13], we assign these to $\text{M}^{\text{II/III}}$ redox processes. The electron-rich complex **P3** shows a second quasi-reversible redox couple at higher potentials which we assign to a $\text{Ru}^{\text{III/IV}}$ redox process. The peak cathodic current, i_{c} , although observable, is much smaller than the peak anodic current, i_{a} .

Compounds **1–4** display quasi-reversible redox couples within the region, $0 \rightarrow -0.5\text{ V}$. For comparison, we recorded the cyclic voltammogram of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{NO})(\text{Cl})]\text{PF}_6$ (**5**) under the same conditions (Fig. 2). Its irreversible nature is typical for that of a competitive decomposition reaction accompanying reduction. Simpson *et al.* [4] have noted the inert nature of the chloride ligand in **5** towards Ag^+ and Tl^+ ions and have found the Ru-Cl bond length to be characteristically shorter than that of its precursor, $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$, [14] which is well known to ionize in polar solvents. We assign the redox processes in **1–4** as $\text{M}^{\text{I/II}}$ couples consistent with electrochemical assignments of other ruthenium(II) nitrosyls [15,16]. With this in mind, we interpret the irreversibility of **5** as due to facile labilization of chloride in the electron-rich reduced state, ruthenium(I), and subsequent coordinating solvation providing irreversible trapping of the chloride free moiety. The displaced oxidative half-couple (Fig. 2) might then be due to the acetonitrile complex, $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{NO})(\text{MeCN})]^+$. The reversibility of **1–4** can therefore be attributed to the inertness of the cyanide ligand, presumably on account of its compensating electronic synergism.

The reaction of sodium azide with **1** is most easily monitored by cyclic voltammetry. As the signal from the $\text{Ru}^{\text{I/II}}$ couple decreases so an irreversible couple is

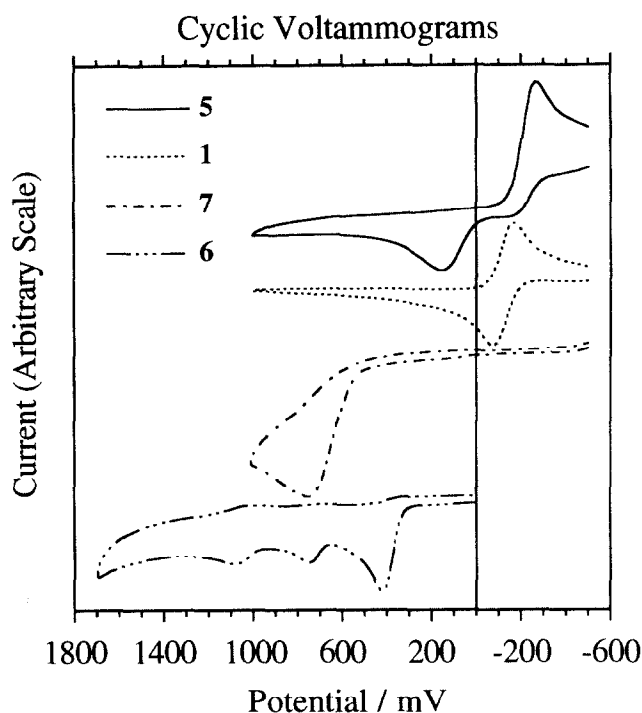


Fig. 2. Cyclic voltammograms of complexes, $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{NO})(\text{Cl})]\text{PF}_6$ (**5**), $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{NO})(\text{CN})]\text{PF}_6$ (**1**), $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{MeCN})(\text{CN})]$ (**7**) and $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{CN})_2]\text{K}$ (**6**); see Table 3 and Experimental section.

formed at *ca.* $+0.8\text{ V}$ (Fig. 2). We assign this to a $\text{Ru}^{\text{II/III}}$ couple in $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{MeCN})(\text{CN})]$ (**7**). Complex **6** shows a similar $\text{Ru}^{\text{II/III}}$ irreversible couple similar to complex **P1**, but at a lower potential on account of the lower π -acidity of the cyanide relative to the phosphine (Fig. 2). The subsidiary peaks at higher potential are presumably processes involving electroactive decomposition products. The profile of the principal oxidative peak was identical to that obtained using a clean electrode scanning between $0 \rightarrow +0.6\text{ V}$.

3. Experimental section

The preparations of **P1**, **P2**, **1** and **2** were carried out in the air and those of the other complexes under nitrogen. The isolation and purification of products was carried out in the air. AnalaR grade solvents were used as supplied. Infrared spectra were recorded at (4 cm^{-1}) , as KBr pellets on a Mattson Polaris FTIR instrument. Nuclear magnetic resonance spectra were recorded on a Bruker AM300 spectrometer (300 MHz , ^1H ; 121.497 MHz , ^{31}P ; 75.468 MHz , ^{13}C). Microanalyses were performed by the Departmental analytical service. Positive-ion Fast-Atom Bombardment (FAB+) mass spectrometry was performed at the SERC

facility, Swansea (UK). Single scan cyclic voltammetry studies were performed on a Princeton Applied Research Potentiostat (Model 273) using dry, distilled acetonitrile (CaH_2), as the solvent with tetrabutylammonium tetrafluoroborate as the base electrolyte (0.2 g/10 ml; $\sim 0.06\text{ M}$). A three-armed single compartment electrochemical cell, consisting of a platinum bead working electrode, a platinum wire counter electrode and a saturated aqueous potassium chloride solution calomel reference electrode, was used. The following compounds were prepared by published procedures; $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ [17], $[(\eta^5\text{-C}_5\text{H}_4\text{-Me})\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ [17], $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ [18], $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{NO})(\text{Cl})]\text{PF}_6$ [4] and $[(\eta^5\text{-C}_5\text{H}_5)\text{Os}(\text{PPh}_3)_2\text{Br}]$ [19].

3.1. Preparation of the complexes

The complexes **P1–P4** and **1–4** were all prepared by the typical syntheses outlined below for **P1** and **1** respectively.

3.1.1. $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{CN}]$ (**P1**)

A mixture of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ (0.25 g, 0.34 mmol) and NaCN (0.125 g, 2.6 mmol) in MeOH (30 ml) was refluxed with stirring. After *ca.* 10 min the orange suspension had been converted into a bright yellow solution. Refluxing was continued for a total of 2 h to ensure complete conversion and the solution then evaporated under reduced pressure to dryness. Following extraction with warm toluene ($\sim 50\text{ ml}$) a white solid was filtered off and washed with a little toluene. The combined toluene extracts were evaporated ($< 60^\circ\text{C}$) to a small volume. The product was isolated by slow addition of an excess of petroleum spirit (40–60), with swirling, until fine yellow crystals had completely separated. If required, recrystallization can be carried out by dissolution in a minimum volume of dichloromethane and precipitation with petroleum spirit. The crystals are collected by filtration, washed with petroleum spirit and vacuum dried.

In the case of the osmium complex **P4**, some purification is necessary to remove dark impurities. The complex is dissolved in a small volume of dichloromethane and adsorbed on a small column of neutral alumina (petroleum spirit). The pure product is eluted with tetrahydrofuran and isolated by evaporation of the eluate to dryness. Yields: **P1** 0.24 g (95%); **P2** (95%); **P3** (50%); **P4** (80%).

3.1.2. $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{NO})(\text{CN})]\text{PF}_6$ (**1**)

The complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{CN}]$ (0.1 g, 0.14 mmol) was dissolved in warm absolute ethanol (15 ml) and the solution was refluxed as hydrochloric acid (0.4 ml, 37%) was added. A solution of sodium nitrite (0.2

g, 2.9 mmol) in water (2 ml) was then added dropwise during 1 min to the refluxing solution, which turned from pale yellow to pale orange. Refluxing was continued for a few minutes and the solution was then cooled to room temperature and filtered. An excess of ammonium hexafluorophosphate (*ca.* 0.7 g) in water (2 ml) was added to the solution, which was then kept at 5°C for 12 h. The orange crystals that separated were filtered off, washed successively with water, ethanol/diethyl ether (1:10), and petroleum spirit (40–60), and vacuum dried. Yields: **1–4** (85%).

3.1.3. $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{CN})_2]\text{Na}$ (**6**)

A solution of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{NO})(\text{CN})]\text{PF}_6$ (0.5 g, 0.79 mmol) in dry deaerated acetonitrile (35 ml) was mixed with one of finely-ground sodium azide (0.06 g, 0.92 mmol) in methanol (5 ml) and the mixture was stirred overnight then evaporated to dryness ($< 50^\circ\text{C}$). The residue was extracted with dichloromethane (20 ml) and the extract filtered, evaporated to small volume ($\sim 3\text{ ml}$), and added immediately to a refluxing solution of sodium cyanide (0.3 g, 6.12 mmol) in methanol (70 ml). The mixture was refluxed for 4 h and then evaporated to dryness, and the product extracted successively with dichloromethane (100 ml), acetonitrile (75 ml), and acetone (100 ml). The washings were combined and taken to dryness again and the residue dissolved in a minimum of methanol and the solution diluted with acetone (10 ml). After filtration to remove some dark impurities, an excess of diethyl ether was slowly added until white needles had completely separated. The crystals were filtered off, washed with a little diethyl ether and petroleum spirit (40–60), and vacuum dried. Yield: **6** 0.2 g (50%).

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