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Trimetallic complexes featuring Group 10 tetracyanometallate dianions as bridging ligands

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Dedicated to Professor D.M.P. Mingos, whose works have been a source of instruction, inspiration and discussion in so many areas of chemistry.

Abstract

The trimetallic complexes {Ru(PPh₃)₂Cp}₂{ μ -M(CN)₄} and {Ru(dppe)Cp*}₂{ μ -M(CN)₄} (M = Ni, Pd, Pt) have been prepared from reactions of RuCl(PPh₃)₂Cp or RuCl(dppe)Cp* with the appropriate tetracyanometallate salt, and structurally characterised. While a similar reaction of FeCl(dppe)Cp with K₂[Pt(CN)₄] afforded {Fe(dppe)Cp}₂{ μ -Pt(CN)₄}, the iron cyanide complex Fe(CN)(dppe)Cp was isolated as the only iron containing product from reaction of FeCl(dppe)Cp with K₂[Ni(CN)₄]. The trimetallic complexes can be oxidised in two sequential one-electron steps. Spectroelectrochemical experiments reveal weak NIR absorption bands in the mono-oxidised complexes which are not present in the binuclear complex K[Ru(dppe)Cp*{Pt(CN)₄}], and are therefore attributed to Ru^{II} \rightarrow Ru^{III} charge transfer processes. The coupling parameter, V_{ab} , extracted using Hush-style analysis falls in the range 250 \pm 50 cm⁻¹, consistent with the weak interaction between the Group 8 metal centres. The energy of the IVCT process is dominated by reorganisation energy of the Group 8 metal–ligand fragment.

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1. Introduction

The cyanide ligand is almost ubiquitous in studies of intramolecular electron transfer in metal complexes. Although the tricentennary of the discovery of Prussian Blue was recently celebrated [1], investigations of cyanide mediated electron transfer continue to raise interest [2], and "designer" derivatives of cyanide bridged polymetallic complexes featuring a wide-variety of molecular frameworks and polygonal structures are a source of considerable research effort driven by the electronic, magnetic and/or photonic properties such materials may offer [3].

The tetracyanometallate dianions derived from Ni(II), Pd(II) and Pt(II) are useful reagents for the assembly of lin-

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ear [4,5], and bent polymetallic complexes [5,6], molecular squares and polyhedra [7] and materials with extended structures [8]. We have recently been drawn to this work as part of a larger study concerned with electron transfer between Group 8 metal centres through unsaturated bridges of general form C_n [9] and $C_n N$ [10], and had cause to consider the influence that the size and electronic structure of the Group 10 metal might play in moderating the interactions between remote metal groups in a mixed valence complex featuring the linear M^(II)-NC-M'-CN- $M^{(III)}$ (M = Fe, Ru; M' = Ni, Pd, Pt) assembly. We report herein descriptions of the syntheses, molecular structures and electrochemical responses of complexes $\{M(PP)Cp'\}_2$ -{ μ -M'(CN)₄} [M = Fe, Ru; PP = (PPh₃)₂, dppe; Cp' = Cp, Cp^* ; M' = Ni, Pd, Pt (not all combinations)], and the characteristics of the mixed-valance complexes that can be derived from them.

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2. Experimental

2.1. General conditions

Reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk methods. No special precautions were taken during work-up and isolation. The complexes RuCl(PPh₃)₂Cp [11], RuCl(dppe)Cp* [12], and FeCl(dppe)Cp [13] were prepared by literature methods. Other reagents were purchased and used as received.

NMR spectra were recorded on Varian Unity-300 (¹H. 299.91 MHz; ³¹P, 121.40 MHz) or INOVA 500 (¹³C, 125.69 MHz) spectrometers from solutions in CDCl₃, and referenced against residual solvent resonances or an external H₃PO₄ reference. Electrochemical measurements were made from solutions in CH₂Cl₂ or THF containing 0.1 M NBu₄BF₄ supporting electrolyte, using a conventional three electrode cell and recorded on an AutoLab PGSTAT-30 potentiostat. A platinum dot working electrode was employed together with Pt wire counter and pseudo reference electrodes. All potentials are reported against SCE, being referenced against an internal ferrocene/ferrocenium [Fc/Fc⁺ = ± 0.46 V versus SCE (CH₂Cl₂) or +0.56 V versus SCE (THF)] or decamethylferrocene/ decamethylferrocenium [Fc*/Fc*⁺ = -0.02 V versus SCE (CH₂Cl₂) or 0.13 V versus SCE (THF)] couples [14]. Spectroelectrochemical studies were carried out in an OTTLE cell of standard design [15], cooled at -30 °C by cold nitrogen gas, using sample solutions (0.1 M NBu₄BF₄/CH₂Cl₂) approximately 0.1 mM in analyte. The reported extinction coefficients have been corrected to allow for the comproportionation equilibria [16].

2.2. General procedure

2.2.1. Preparation of $[\{RuL_2Cp'\}_2 \{\mu - M(CN_4)\}] (L = PPh_3, Cp' = Cp; L_2 = dppe, Cp' = Cp^*; M = Ni, Pd, Pt)$

A 50 ml, two-necked Schlenk flask was charged with $K_2[M(CN)_4]$ (0.208 mmol) and $RuClL_2Cp'$ (0.415 mmol). The mixture was suspended in MeOH (30 ml) and heated at reflux for 1 h, after which time the solution was cooled and the precipitate was collected and washed with cold methanol to afford [{RuL}_2Cp'}_2{\mu-M(CN_4)}] as a bright yellow solid, which was purified by column chromatography (alumina). Crystals of compounds **1a**–**c** suitable for X-ray diffraction studies were obtained by slow diffusion of MeOH into a CH₂Cl₂ solution. Crystals of compounds **2a** and **2c** suitable for X-ray diffraction studies were obtained by slow diffusion. Crystals of compounds **2a** and **2c** suitable for X-ray diffraction studies were obtained by slow diffusion of EtOH into CHCl₃ solutions. Crystals of compound **2b** were obtained by slow diffusion of EtOH into a CH₂Cl₂ solution.

2.2.2. $[{Ru(PPh_3)_2Cp}_2{Ni(CN)_4}]$ (1a)

(0.149 mmol, 72%). Found: C, 65.78; H, 4.52; N, 3.59. C₈₆H₇₀P₄N₄Ru₂Ni · 0.5(CH₂Cl₂) requires: C, 65.48; H, 4.51; N, 3.53. ¹H NMR: δ 4.29 (s, 10H, Cp); 7.30–7.25 (m, 72 H, PPh₃). ¹³C NMR: δ 137.4 (m, $J_{CP} = 22$ Hz, C_{ipso}); 133.8 (t, $J_{CP} = 5$ Hz, C_{ortho}); 129.3 (s, C_{para}); 128.3 (t, $J_{CP} = 5$ Hz, C_{meta}); 83.4 (s, Cp). ES(+)-MS (m/z): 1568 [M + Na]⁺, 691 [Ru(PPh₃)₂Cp]⁺.

2.2.3. $[{Ru(PPh_3)_2Cp}_2{Pd(CN)_4}]$ (1b)

(0.100 mmol, 48%). Found: C, 63.38; H, 4.39; N, 3.57. $C_{86}H_{70}P_4N_4Ru_2Pd \cdot 0.5CH_2Cl_2$ requires: C, 63.56; H, 4.38; N, 3.43. ¹H NMR: δ 4.30 (s, 10H, Cp); 7.33–7.10 (m, 72 H, PPh₃). ¹³C NMR: δ 136.0 (m, $J_{CP} = 20$ Hz, C_{ipso}); 132.5 (t, $J_{CP} = 5$ Hz, C_{ortho}); 128.1 (s, C_{para}); 127.0 (t, $J_{CP} = 5$ Hz, C_{meta}); 82.2 (s, Cp). ES(+)-MS (m/z): 1614, $[M + Na]^+$; 691, $[Ru(PPh_3)_2Cp]^+$.

2.2.4. $[{Ru(PPh_3)_2Cp}_2{Pt(CN)_4}]$ (1c)

(0.095 mmol, 46%). Found C, 60.64; H, 4.12; N, 3.37. $C_{86}H_{70}P_4N_4Ru_2Pt \cdot 0.5(CH_2Cl_2)$ requires: C, 60.30; H, 4.15; N, 3.25. ¹H NMR: δ 4.30 (s, 10H, Cp); 7.30–7.26 (m, 72 H, PPh₃). ¹³C NMR: δ 137.3 (m, $J_{CP} = 22$ Hz, C_{ipso}); 133.7 (t, $J_{CP} = 5$ Hz, C_{ortho}); 129.4 (s, C_{para}); 128.3 (t, $J_{CP} = 4$ Hz, C_{meta}); 83.4 (s, Cp). ES(+)-MS (m/z): 1705 [M + Na]⁺; 691 [Ru(PPh_3)_2Cp]⁺.

2.2.5. $[{Ru(dppe)Cp^*}_2{Ni(CN)_4}]$ (2a)

(0.129 mmol, 68%). Found: C, 63.37; H, 5.45; N, 3.97. $C_{76}H_{78}P_4N_4Ru_2Ni$ requires: C, 63.74; H, 5.49; N, 3.91. ¹H NMR: δ 1.45 (s, 15H, Cp*); 2.06, 2.62 (m, 4H, dppe); 7.15–7.70 (m, 20H, Ph). ¹³C NMR: δ 142.9 (s, CN); 136.9 (m, C_{ipso}); 134.2 (m, C_{ipso}); 133.6 (m, 2 × C_{ortho}); 130.0 (s, CN); 129.9 (s, C_{para}); 129.7 (s, C_{para}); 128.6 (t, $J_{CP} = 5$ Hz, C_{meta}); 128.0 (t, $J_{CP} = 5$ Hz, C_{meta}); 91.7 (s, C_5Me_5); 28.8– 28.4 (m, dppe); 10.1 (s, C_5Me_5). ES(+)-MS (*m*/*z*): 1433 [M + H]⁺; 635 [Ru(dppe)Cp*]⁺.

2.2.6. $[{Ru(dppe)Cp^*}_2 {Pd(CN)_4}] (2b)$

(0.068 mmol, 37%). Found: C, 60.81; H, 5.25; N, 3.70. $C_{76}H_{78}P_4N_4Ru_2Pd \cdot 2(C_2H_5OH)$ requires: C, 61.21; H, 5.77; N, 3.56. ¹H NMR: δ 1.48 (s, 15H, Cp*); 2.00, 2.57 (m, 4H, dppe); 7.10–7.70 (m, 20H, Ph). ¹³C NMR: δ 140.9 (s, CN); 136.7 (m, C_{ipso}); 134.0 (m, C_{ipso}); 133.64 (t, $J_{CP} = 5$ Hz, C_{ortho}); 133.5 (t, $J_{CP} = 5$ Hz, C_{ortho}); 130.0 (s, C_{para}); 129.8 (s, C_{para}); 128.7 (t, $J_{CP} = 5$ Hz, C_{meta}); 128.0 (t, $J_{CP} = 5$ Hz, C_{meta}); 127.2 (s, CN); 91.7 (s, C_5Me_5); 28.8–28.4 (m, dppe); 10.1 (s, C_5Me_5). ES(+)-MS (m/z): 1481 [M + H]⁺; 635 [Ru(dppe)Cp*]⁺.

2.2.7. $[{Ru(dppe)Cp^*}_2{Pt(CN)_4}]$ (2c)

(1.08 mmol, 57%). Found: C, 58.16; H, 4.98; N, 3.54. $C_{76}H_{78}P_4N_4Ru_2Pt$ requires: C, 58.19; H, 5.01; N, 3.57. ¹H NMR: δ 1.48 (s, 15H, Cp*); 2.08, 2.63 (m, 4H, dppe), 7.15–7.75 (m, 20H, Ph). ¹³C NMR: δ 136.7 (m, C_{ipso}); 134.0 (m, C_{ipso}); 133.7 (t, $J_{CP} = 5$ Hz, C_{ortho}); 133.6 (s, CN); 133.5 (t, $J_{CP} = 5$ Hz, C_{ortho}); 130.0 (s, C_{para}); 129.8 (s, C_{para}); 128.7 (t, $J_{CP} = 5$ Hz, C_{meta}); 128.0 (t, $J_{CP} = 4$ Hz, C_{meta}); 121.6 (s, CN); 91.7 (s, C₅Me₅); 28.8–28.5 (m, dppe); 10.1 (s, C₅Me₅). ES(+)-MS (*m*/*z*): 1569 [M + H]⁺; 635 [Ru(dppe)Cp*]⁺.

2.2.8. $K[Ru(dppe)Cp^*{Pt(CN)_4}]$ (3)

A 50 ml, two-necked Schlenk flask was charged with $K_2[Pt(CN)_4]$ (127 mg, 0.337 mmol) and $RuCl(dppe)Cp^*$ (150 mg, 0.224 mmol). The mixture was suspended in MeOH (10 ml) and heated at reflux for 1.5 h after which time the solution was cooled and the solvent removed. The yellow residue was dissolved in the minimum quantity of CH_2Cl_2 and filtered. Removal of solvent afforded **3** as a yellow powder (168 mg. 0.172 mmol, 77%). Found: C, 48.85; H, 4.07; N, 5.28. $C_{40}H_{39}P_2N_4RuPtK$ requires: C, 49.38; H, 4.04; N, 5.76. ¹H NMR: δ 1.47 (s, 15H, Cp*); 2.08, 2.64 (m, 4H, dppe); 7.20–7.68 (m, 20H, Ph). ES(+)-MS (m/z): 635 [Ru(dppe)Cp*]⁺. ES(-)-MS (m/z): 932 [Ru(dppe)Cp*{Pt(CN)_4}]⁻; 273 [Pt(CN)_3]⁻.

2.2.9. $[{Fe(dppe)Cp}_{2}{Pt(CN)_{4}}]$ (4c)

A 50 ml, two-necked Schlenk flask was charged with $K_2[Pt(CN)_4]$ (102 mg, 0.27 mmol) and FeCl(dppe)Cp (300 mg, 0.54 mmol). The mixture was suspended in MeOH (30 ml) and heated at reflux for 90 min after which time reaction was cooled and the solvent removed. The residue was then dissolved in a minimum volume of CH₂Cl₂, filtered, loaded onto a silica column and eluted with 60:40 acetone:hexane. The resultant red band was collected and the solvent removed. Subsequent crystallisation from slow diffusion of MeOH into a CH₂Cl₂ solution resulted in the formation of 4c as red crystals (156 mg, 0.12 mmol, 43%). ¹H NMR: δ 2.08, 2.63 (2 × br, 4H, dppe); 4.19 (s, 5H, Cp); 7.20–7.79 (m, 20H, Ph).

2.3. Crystallography

Diffraction data were collected on Bruker three-circle diffractometers with SMART 6K (for 1c), SMART 1K (for 1a, 1b and 2c) or APEX (for 2a and 2b) CCD area detectors, using graphite-monochromated sealed-tub Mo K α radiation. The data collection was carried out at 120 K using cryostream (Oxford cryosystem) open flow N₂ cryostats. Reflection intensities were integrated using the SAINT V6.22 program [17], for 2a–c, and SAINT V6.02a [18] for 1a–c.

The crystal structures were solved using direct-methods and refined by full matrix least-squares against F^2 of all data using SHELXTL [19] software. All non-hydrogen atoms where refined in anisotropic approximation, except a chlorine atom of a dichloromethane molecule in **1b**, which was isotropically refined. Hydrogen atoms were either located by a difference map (for 2a-c) or placed in calculated positions (1a-c) and refined isotropically using a riding model. Solvent molecules were initially present in all the structures, and in cases where all or some of the solvent molecules were disordered (for 1a, 2b and 2c) Platon's Squeeze [20] tool was applied to remove them. Thus, in **1a** approximately four molecules of dichloromethane molecules per unit cell were removed, resulting in a total of ca. 152.5 e⁻ within the void volume, as calculated by Squeeze, and leaving no molecules of the crystallisation solvent in the final refined crystal structure. In **2b**, the Squeeze tool was also applied to remove approximately six disordered dichloromethane molecules per unit cell, giving a total of ca. $244.9 e^-$ within the void volume, and leaving two ordered ethanol molecules per formula unit, which are hydrogen bonded to cyanide groups. In **2c**, Squeeze was applied to remove approximately six disordered chloroform molecules per unit cell, giving a total of ca. $357.8 e^-$ within the void volume, and leaving two molecules of ethanol per formula unit, which are hydrogen bonded to cyanide groups in a manner similar to that in **2b**. Crystal data and experimental details are listed in Table 2.

3. Results and discussion

The compounds 1a-c and 2a-c were prepared by reaction of the half-sandwich metal chlorides $RuCl(PPh_3)_2Cp$ or $RuCl(dppe)Cp^*$ with one half-equivalent of the appropriate potassium tetracyanometallate (Scheme 1). The KCl by-product was removed by extraction and filtration, and the pure trimetallic compounds were obtained as yellow crystalline solids in moderate to good yield after column chromatography and crystallisation.

The compounds were readily characterised from solution spectroscopic data (Table 1). In each case the IR spectrum clearly revealed two $v(C \equiv N)$ bands which were assigned to bridging $(2136-2157 \text{ cm}^{-1})$ and non-bridging $(2118-2130 \text{ cm}^{-1})$ CN moieties by comparison with the spectra of the precursor $K_2[M(CN)_4]$ species (Table 1). The Cp and Cp* ligands gave rise to the expected resonances in the ¹H and ¹³C NMR spectra, with additional resonances arising from the phosphine ligands. The ${}^{31}P$ NMR spectra were also unremarkable and simply served to confirm the presence of the phosphine ligands. The complexes co-crystallised with solvent, and the tenacity of the crystalline samples to retain portions of these solvents was apparent in the microanalytical results. The positiveion electrosopray mass spectra (ES(+)-MS) displayed isotopic envelopes arising from the $[M + Na]^+$ (1a-b) or $[M + H]^+$ ions (2a-c) as well as fragment ions corresponding to the $[Ru(PPh_3)_2Cp]^+$ and $[Ru(dppe)Cp^*]^+$ at m/z 691 and 635, respectively.

The bimetallic anion $[\text{Ru}(\text{dppe})\text{Cp}^*{\text{Pt}(\text{CN})_4}]^-$ was obtained as its potassium salt (3) from a 1.5:1 reaction of $K_2[\text{Pt}(\text{CN})_4]$ with RuCl(dppe)Cp* in refluxing methanol, with subsequent work-up affording the material as a powder. This salt was characterised by the usual spectroscopic techniques (Table 1), including negative-ion electrospray mass spectrometry (ES(-)-MS), which displayed isotopic envelopes at m/z = 932 ([Ru(dppe)Cp*{Pt(CN)_4}]⁻) and 273 ([Pt(CN)_3]⁻). Infra-red spectroscopy revealed a single v(C=N) band at 2130 cm⁻¹.

With a range of ruthenium complexes in hand, analogous species featuring the more electron-rich/ π -donating [Fe(dppe)Cp]⁺ fragment were also sought. Reaction of the iron complex FeCl(dppe)Cp with K₂[Pt(CN)₄] in refluxing methanol (90 min) resulted in the formation of



Scheme 1. Synthesis of $[{Ru(L)Cp'}_2{\mu-M(CN)_4}]$.

 Table 1

 Selected spectroscopic data for compounds 1a-c, 2a-c, 3 and 4c

Compound	$v(CN)/cm^{-1}$	δ (Cp or Cp*) (¹ H/ ¹³ C)	$\delta(PR_3)$	
$K_2[Ni(CN)_4]$	2124 ^a			
$K_2[Pd(CN)_4]$	2136 ^a			
$K_2[Pt(CN)_4]$	2133 ^a			
1a	2143, 2119	4.29/83.43	43.40	
1b	2157, 2130	4.30/82.16	43.21	
1c	2157, 2129	4.30/83.43	43.12	
2a	2136, 2118	1.45/91.68, 10.08	71.71	
2b	2146, 2129	1.48/91.68, 10.13	75.79	
2c	2150, 2128	1.48/91.70, 10.07	75.73	
3	2130	1.47/90.40, 8.79	75.67	
4c	2149, 2128	4.19/-	100.34	

^a In water [22].

a red solution from which [{Fe(dppe)Cp}₂{ μ -Pt(CN)₄}] (4c) was obtained as a red crystalline solid in 43% isolated yield. This method of preparation is a minor modification of that described previously by the Vahrenkamp group, which involved the reaction of PPN₂[Pt(CN)₄] with FeCl(dppe)Cp in CH₂Cl₂ for 3 days to afford 4c in 72% yield [5]. The lower yield of the reaction reported here is counterbalanced by the shorter reaction time and the commercial availability of the potassium tetracyanoplatinate reagent.

Attempts to form complexes $[{Fe(dppe)Cp}_2{\mu M(CN)_4$ [M = Ni (4a), Pd (4b)] using similar conditions were not so successful. Reaction of FeCl(dppe)Cp with $K_2[Ni(CN)_4]$ in refluxing methanol resulted in a red/orange solution from which orange crystals were obtained upon work-up. Spectroscopic analysis of this material revealed a single $v(C \equiv N)$ band in the IR spectrum at 2063 cm⁻¹ as well as ¹H NMR resonances at 4.31 ppm (Cp) and broad signals at 2.62 and 2.37 ppm (dppm). Comparison of these data with literature values [10a,21], revealed this compound to be Fe(CN)(dppe)Cp (5), formed by cyanide ligand abstraction from the nickel precursor and isolated in ca. 40% yield. The relatively high yield precludes the notion that 5 is formed from trace amounts of KCN present in the nickel reagent. Reaction of FeCl(dppe)Cp with $K_2[Pd(CN)_4]$ in refluxing methanol resulted in a red/orange powder, with IR spectroscopy revealing $v(C \equiv N)$ bands at 2134 and 2127 cm⁻¹, consistent with $[{Fe(dppe)Cp}_2 \{Pd(CN)_4\}$ (4b), as well as a band arising from

Fe(CN)(dppe)Cp at 2063 cm⁻¹. Attempts to separate this mixture have, as yet, been unsuccessful.

3.1. Molecular structures

The structure of each of the ruthenium complexes 1a-c, 2a-c was determined by X-ray diffraction studies, the structure of 4c having already been reported [5]. The crystallographic data are summarised in Table 2, whilst selected bond lengths and bond angles are summarised in Tables 3 and 4. A representative molecular structure is shown in Fig. 1, illustrating the atom labelling scheme.

For each compound, the Group 10 metal sits on a centre of inversion in the molecule, and as such for any given complex the parameters at each Group 8 metal centre are identical. The geometry about the ruthenium centres is not unusual. The geometry about the central metal M (M = Ni, Pd, Pt) is square planar, with the sum of angles C(1)–M–C(2) being 360°. Direct comparisons of the metrical parameters about the Group 10 metal are complicated by the different size of the metal atoms. The effective ionic radii of square planar Ni²⁺, Pd²⁺ and Pt²⁺ are 0.49, 0.64 and 0.60 Å, respectively [23], and when allowance is made for this variation the experimentally determined M–C(1) and M–C(2) bond lengths display no statistically significant difference.

The Ru–N(2) bond lengths for in **2a–c** [2.037(3)–2.049(2) Å] are marginally shorter than those in **1a–c** [2.060(8)-2.069(3) Å], probably a consequence of electrostatic factors. Similar effects are observed on the Ru–N bonds in benzonitrile complexes of these same RuL₂Cp' fragments [24]. Attachment of the Group 8 metal centre has little effect on the CN moiety, there being no significant variation in the C(1)–N(1) and C(2)–N(2) bond lengths across the series. While the M–C(2)–N(2) bond angles are close to linear, there is a greater deviation from linearity in the Ru–N(2)–C(2) bond angles (Table 4). Similar effects have been observed in other cyanide-bridged species, and generally attributed to the differences in π -back-bonding at the C and N termini of the cyanide moiety.

The crystal structure of the iron/platinum complex 4c has been reported previously [5]. As with the ruthenium complexes this structure was found to be centrosymmetric about the [M(CN)₄] moiety. The only differences of note in

Table 2 Crystallographic details for compounds **1a–c** and **2a–c**

Compound	1a	1b	1c	2a	2b	2c
Formula	$C_{86}H_{70}N_4P_4$ -	$C_{86}H_{70}N_4P_4Ru_2Pd\cdot\\$	$C_{86}H_{70}N_4P_4Ru_2Pt\cdot\\$	C ₇₆ H ₇₈ N ₄ P ₄ Ru ₂ -	$C_{76}H_{78}N_4P_4Ru_2P\cdot\\$	$C_{76}H_{78}N_4P_4Ru_2Pt\cdot \\$
	Ru ₂ Ni	2CH ₂ Cl ₂ /2MeOH	2CH ₂ Cl ₂ /2MeOH	Ni2CHCl ₃	$2C_2H_5OH$	$2C_2H_5OH$
M	1544.19	1825.82	1914.51	1551.5	1572	1661
a (Å)	9.8590(3)	10.5596(10)	10.5697(5)	11.3214(10)	8.5279(8)	8.5326(12)
<i>b</i> (Å)	23.3226(7)	22.500(2)	22.5080(9)	12.3886(11)	24.917(2)	25.012(3)
<i>c</i> (Å)	17.7015(5)	17.1648(13)	17.1733(7)	14.3895(11)	19.1022(16)	20.777(3)
α (°)	90	90	90	71.639(3)	90	90
β (°)	92.1780(10)	99.559(6)	99.628(2)	75.692(4)	90.971(4)	113.577(5)
γ (°)	90	90	90	78.916(4)	90	90
$V(\text{Å}^3)$	4067.3(2)	4021.6(6)	4028.0(3)	1841.6(3)	4058.5(6)	4064.0(10)
$\rho (mg/m^3)$	1.261	1.508	1.578	1.507	1.286	1.357
<i>T</i> (K)	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	P2(1)/n	P2(1)/n	P2(1)/n	$P\bar{1}$	P2(1)/n	P2(1)/c
Z	2	2	2	1	2	2
$\mu ({\rm mm}^{-1})$	0.718	0.856	2.366	1.009	0.710	2.207
Reflections collected	29102	45343	43801	22020	50442	28 553
Independent reflections [<i>R</i> _{int}]	10001 [0.0594]	10830 [0.0987]	12290 [0.0559]	10996 [0.0276]	12325 [0.0281]	11443 [0.1025]
Goodness-of-fit (on F^2)	1.177	1.003	1.028	1.127	1.079	0.936
$R [F, I > 2\sigma(I)]$ wR (F ² , all data)	0.1001, 0.2149	0.0544, 0.1281	0.0424, 0.1132	0.0563, 0.1532	0.0304, 0.0800	0.0745, 0.1732

Table 3 Selected bond lengths (Å) for the complexes 1a-c, 2a-c and 4c [5]

Compound	Ru–N(2)	N(2)-C(2)	M-C(2)	M-C(1)	C(1)–N(1)	Ru-P(1)	Ru–P(2)
1a	2.060(6)	1.151(9)	1.871(7)	1.885(8)	1.129(10)	2.317(2)	2.3333(19)
1b	2.069(3)	1.141(5)	2.002(4)	2.010(5)	1.133(6)	2.3160(12)	2.3221(11)
1c	2.065(3)	1.150(5)	1.994(4)	1.991(4)	1.149(5)	2.3183(9)	2.3231(9)
2a	2.037(3)	1.148(5)	1.854(4)	1.875(4)	1.148(5)	2.2922(9)	2.3127(9)
2b	2.048(2)	1.149(2)	1.990(2)	2.004(2)	1.148(3)	2.2783(5)	2.2927(5)
2c	2.049(6)	1.139(9)	1.992(7)	2.004(9)	1.170(10)	2.293(2)	2.275(2)
4c ^a	1.914(5)	1.131(8)	1.993(6)	1.990(8)	1.153(10)	2.210(2)	2.202(2)

^a For Ru read Fe.

Table 4

Selected bond angles (°) for the complexes $1a{-}c,\,2a{-}c$ and 4c [5]

Compound	Ru–N(2)–C(2)	N(2)-C(2)-M	M-C(1)-N(1)	C(1)-M-C(2)	C(2)-M-C(1')	P(1)-Ru-P(2)
1a	169.1(6)	177.1(6)	178.7(8)	93.0(3)	87.0(3)	101.11(7)
1b	171.3(4)	178.4(4)	177.2(5)	88.5(2)	91.5(2)	100.74(4)
1c	171.0(3)	178.2(3)	177.6(4)	88.7(1)	91.3(1)	100.68(3)
2a	169.2(3)	172.5(3)	177.3(3)	88.0(2)	92.0(2)	82.65(3)
2b	175.82(14)	174.6(2)	177.8(2)	91.55(7)	88.45(7)	82.87(2)
2c	174.7(6)	175.9(6)	177.1(7)	91.3(3)	88.7(3)	82.81(7)
4c ^a	168.5(5)	176.0(6)	178.8(7)	91.8(2)	88.2(2)	85.59(7)

^a For Ru read Fe.

the structure of 4c when compared with the ruthenium analogues 1c and 2c arise from the smaller size of the iron centre, which results in shortening of the Fe–N and Fe–P distances relative to the Ru–N and Ru–P. In summary, the molecular structures of the compounds 1a-c, 2a-c and 4c are similar. There is no variation in the C(2)–N(2) bond lengths that might be expected to reflect variation in back-bonding interactions, nor is there any change in

the C(2)–M bond lengths with variation of M' (M' = Ni, Pd, Pt).

3.2. Electrochemistry

The great interest in the properties of compounds in which redox active groups are separated by some bridging moiety prompted an examination of the tetracyanometallate



Fig. 1. A plot of a molecule of $[{Ru(dppe)Cp}_{2}{\mu-Pd(CN)_{4}}]$ (2b) showing the atom labelling scheme, which is representative of that used in the series 1a-c, 2a-c.

bridged complexes **1a–c**, **2a–c** and **4c** by cyclic and differential pulse voltammetry (Table 5).

For compounds **1a–c**, **2a–c** and **4c**, two oxidation events were observed at a platinum electrode. Whilst these events were fully chemically and electrochemically reversible at room temperature for compounds **2a–c** and **4c**, sub-ambient temperatures ($-30 \circ C$) were required to improve the chemical reversibility of these anodic processes for **1a–c**. The small difference between the half-wave potentials, ΔE , necessitated that in some cases differential pulse voltammetry be used to determine this parameter more accurately. The electrochemical response of the bimetallic anion **3** was characterised by a single reversible oxidation at 0.74 V. The lower oxidation potentials of the compounds **2a–c** relative to **1a–c** can be attributed to the variations

Table 5

Electrochemical data, given against SCE by correction against internal ferrocene/ferrocinium or decamethylferrocene/decamethylferrocinium couples

Compound	$E_{1/2}(1)$ (V)	$E_{1/2}(2)$ (V)	$\Delta E_{1/2}$ (V)	$K_{\rm c}^{\rm c}$
1a ^a	0.95	1.06	0.11	190
1a ^b	1.11	1.20	0.09	75
1b ^a	1.00	1.08	0.08	45
1b ^b	1.14	1.20	0.06	20
1c ^a	0.97	1.08	0.11	190
1c ^b	1.08	1.20	0.12	310
2a ^a	0.69	0.82	0.13	155
2a ^b	0.81	0.90	0.09	35
2b ^a	0.72	0.84	0.12	105
2b ^b	0.82	0.90	0.08	20
2c ^a	0.71	0.85	0.14	230
2c ^b	0.82	0.92	0.10	50
3 ^a	0.74	n/a	n/a	n/a
4c ^a	0.34	0.45	0.11	70

^a CH₂Cl₂.

^b THF.

^c $K_c = \exp{\{\Delta E_{ox}F/RT\}}$, where $F/RT = 47.76 \text{ V}^{-1}$ at 243 K (1a–c) and 38.92 V⁻¹ at 298 K (2a–c).

in the supporting ligands. Unsurprisingly, the very electron-rich iron end-caps in **4c** result in the lowest oxidation potentials observed across the series.

A variety of solvation factors and ion-paring phenomena can influence oxidation potentials, and this point has recently been highlighted by Keene as a potential complication in the determination of "electronic coupling" on the basis of electrochemical measurements alone [25]. The electrochemical responses of 1a-c and 2a-c were recorded in two different solvents in an effort to distinguish through-bond from through-space effects. In general, the difference between the two oxidation potentials $(\Delta E_{1/2})$ is somewhat smaller in THF than CH₂Cl₂, with the decreased separation of the oxidation potentials arising from the greater relative shift of the first oxidation event to higher potentials. Thus, it would appear that there is some contribution to the thermodynamic stability of the one-electron oxidation products arising from solvation factors. The redox behaviour of compounds 1c and **4c** have already been described by Vahrenkamp [5], with two successive oxidations being observed at +0.89 and +0.99 V and +0.36 V and +0.47 V, respectively, relative to Ag|AgCl.

The bimetallic complex 3 only exhibits a single anodic event within the potential window accessible in CH_2Cl_2 . The most closely related trimetallic complex, 2c, is more readily oxidised than 3, despite the anionic charge on the latter. Taken together, these observations point to some interaction between the Group 8 metal centres.

3.3. Mixed-valence complexes

The electronic spectra of the oxidised versions of the complexes in this study would be expected to show IVCT bands characteristic of the metal-metal interactions, as demonstrated for 4c [5]. Furthermore band shape analysis would be expected to reveal the extent of the communication between the metal centres and any trends that occur as a function of the central metal would become apparent. While the mixed-valence derivative $[4c]^+$ and the dication $[4c]^{2+}$ have been prepared by stoichiometric oxidation of 4c with AgPF₆, and the spectroscopic properties of these species studied in detail [5], for convenience we chose to use spectro-electrochemical methods to analyse the other compounds in the series.

The UV–Vis–NIR spectra were collected from CH₂Cl₂ solutions approximately 0.1 mM in analyte and contain-

Table 6 UV–Vis spectroscopic data for compounds **2a–c**, **3** and **4c** [5]

Compound	$\overline{v}_{\text{max}}/\text{cm}^{-1}$ and $(\epsilon/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1})$
2a	32680 (12280); 25900 (3900)
2b	31 250 (3860); 27 250 (2480)
2c	31 060 (14 540); 26 390 (3920)
3	31150 (2680); 26460 (1370)
4c	29850 (8673); 21740 (1360); 19690 (1120)

Table 7 NIR spectroscopic parameters and associated values from $[2a]^+$, $[2b]^+$, and $[2c]^+$

Compound	$\bar{v}_{max}~(cm^{-1})$	$\Delta \bar{\nu}_{1/2(calc)}~(cm^{-1})$	$\Delta \bar{\nu}_{1/2(found)}~(cm^{-1})$	$\varepsilon \;(\mathrm{mol}^{-1} \;\mathrm{dm}^3 \;\mathrm{cm}^{-1})$	r (Å)	$V_{\rm ab}$	λ
[2a] ⁺	6380	3800	4800	730	10.00	300	5300
[2b] ⁺	6780	4000	4000	500	10.35	230	5800
[2c] ⁺	5680	3600	5100	530	10.34	250	4900
[4c] ⁺	6410	3560	4720	600	10.00	270	5520

ing 0.1 M [NBu₄]BF₄ as a supporting electrolyte. Whilst on the CV timescales (<10 s) the anodic events from the whole series were chemically reversible, the first oxidation states of **1a** and **1b** were insufficiently reversible on the longer timeframe required for bulk electrolysis in the OTTLE cell for acquisition of meaningful spectra. Therefore, in the interests of obtaining a complete data set, only the Ru(dppe)Cp* derived complexes **2a**-c were studied in detail. However, even in these cases, only the first oxidation product could be obtained with complete reversibility and then only at sub-ambient temperatures (-30 °C).

The neutral compounds 2a-c and 3 displayed two absorption bands in the UV (35000–20000 cm⁻¹) region of the spectrum, the lower energy band appearing as a shoulder. Compound 4c displays an absorption band at 29850 cm⁻¹ as well as a broader absorption envelope with apparent band maxima at 21740 and 19690 cm⁻¹ (Table 6).

Upon oxidation of 2a-c, these electronic absorption bands moved to slightly lower energy, while in contrast oxidation of 4c resulted in the reverse behaviour was seen. Oxidation of the bimetallic complex 3 gave a new absorption band at 20330 cm⁻¹.

In addition to the bands already described, an absorption band envelope was observed in the NIR region of the spectra of the trimetallic cations $[2a]^+$, $[2b]^+$ and $[2c]^+$. The high energy side of this absorption envelope overlapped the tails of bands from the higher energy end of the visible spectrum. Critically, the NIR region of 3 remained transparent during the oxidation and therefore the NIR absorptions observed in $[2a]^+$, $[2b]^+$ and $[2c]^+$ can be confidently assigned to a genuine Ru^{II}/Ru^{III} IVCT transition.

The NIR band in $[2a]^+$, $[2b]^+$, $[2c]^+$ is well approximated by a single Gaussian-shaped curve, which is broader than that calculated from the Hush expression (Eq. (1)), suggesting that each complex is well described a classical Class 2 mixed-valence complex

$$\Delta \bar{v}_{1/2} = (2310\bar{v}_{\text{max}})^{1/2}.$$
 (1)

Assuming the crystallographically determined Ru–Ru separation approximates the electron-transfer distance, r, modest coupling parameters, V_{ab} , are calculated in the following equation (Table 7):

$$V_{\rm ab} = \frac{0.0205 (\varepsilon \bar{\nu}_{\rm max} \Delta \bar{\nu}_{1/2})^{1/2}}{r}.$$
 (2)

The reorganisation energy associated with the electrontransfer process, λ , can be estimated from the electrochemical and spectroscopic data, with

$$\mathcal{A} = \bar{\nu}_{\text{max}} - 8064\Delta E_{1/2}.\tag{3}$$

The electronic parameters extracted from the spectroscopic data show little sensitivity to the nature of the central metal, and given the approximations made, the metal-metal coupling or "communication" in these systems are identical, and, as noted by Vahrenkamp for related systems, the energy of the IVCT band depends heavily on the reorganisation energies and coupling parameters are similar, displaying less than $\pm 10\%$ variation with the change in Group 10 metal atom, suggesting that the nature of the Group 8 metal containing fragment and the through-space electron-transfer distance are predominant factors in the electron-transfer process.

4. Conclusion

The tetracyanometallates of the Group 10 metals are convenient dianionic metalloligands, and readily give rise to linear trimetallic complexes. Oxidation of the complexes $\{Ru(dppe)Cp^*\}_2\{\mu-M(CN)_4\}$ affords Class 2 mixedvalence complexes, which demonstrate electron-transfer over distances of ca. 10 Å. A combination of electrochemical and spectroelectrochemical studies reveal the energy of the photoinduced electron-transfer process to be dependent on the reorganisation energy of the terminal Group 8 metal fragments and the through-space separation.

5. Supporting information

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 280645–280650 for compounds **1a**—c, **2a**–c, respectively. Copies of this information may be obtained free of charge from The Director CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (fax (int code): +44 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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