DALTON
FULL PAPER

Synthesis and characterisation of unsymmetrical metal (Ru$^{\mathrm{II}}$, Os$^{\mathrm{II}}$) and ferrocenyl complexes of 1,3,5-triethynylbenzene

Nicholas J. Long,[*a] **Angela J. Martin,**[a] **Andrew J. P. White,**[a] **David J. Williams,**[a]
Marco Fontani,[b] **Franco Laschi**[b] **and Piero Zanello**[b]

[a] *Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London, UK SW7 2AY*
[b] *Dipartimento di Chimica, del l'Universita di Siena, Via Aldo Moro, 53100 Siena, Italy*

Received 28th June 2000, Accepted 18th August 2000
First published as an Advance Article on the web 18th September 2000

A series of complexes featuring metal (*trans*-[RuCl(dppm)$_2$], *trans*-[OsCl(dppm)$_2$] or [Ru(η-C$_5$H$_5$)(PPh$_3$)$_2$]) and ferrocenyl (C$_5$H$_5$FeC$_5$H$_4$) units unsymmetrically arranged around the periphery of a 1,3,5-triethynylbenzene core have been synthesized in good to reasonable yields by various synthetic routes. A crystal structure determination of *trans*-[(C$_5$H$_5$FeC$_5$H$_4$C$\equiv$C)$_2$C$_6$H$_3${C$\equiv$CRu(dppm)$_2$Cl}] shows that the two ferrocenyl units are positioned on the same side of the trisubstituted aromatic core and that all three ethynyl linkages are bent 'down' out of the plane of the central ring. Electrochemical studies show that in the heteronuclear coupling of osmium(II) or ruthenium(II) fragment(s) with ferrocenyl unit(s) the oxidation of Os$^{\mathrm{II}}$ or Ru$^{\mathrm{II}}$ precedes that of the ferrocene unit(s). In addition, whereas in diruthenium or diosmium complexes the oxidation of the two metal centres proceeds separately, in the diferrocenyl complexes the oxidation of the two ferrocene units occurs at the same potential values. This result shows that on appending different groups to the same skeletal core (namely, triethynylbenzene) some can interact electronically (the Ru$^{\mathrm{II}}$- and Os$^{\mathrm{II}}$-containing fragments) whereas others do not (the ferrocenyl units).

Introduction

Carbon-rich organometallics containing rigid, π-conjugated chains are of increasing interest due to their uses in the syntheses of unsaturated organic species,[1] organometallic polymers[2] and π-conjugated bi- or multi-metallic systems.[3] A central triethynylbenzene core is of particular interest due to its geometry and active co-ordination sites which enables simple dehydrohalogenation reactions to be used in order to extend the core in three directions thus building up a first generation dendrimer.[4] Other recent examples featuring this core unit have involved the incorporation of [Fe(η-C$_5$Me$_5$)(dppe)],[5] [IrCl(PPh$_3$)$_2$(CO)(MeCN)],[6] [Cr(η-C$_6$H$_6$)(CO)$_3$],[7] [Ru(bpy)$_2$(phen)]$^{2+}$,[8] [Au(PR$_3$)],[9] [PtCl(XBu$^{\mathrm{n}}_3$)$_2$] (X = P or As),[3f] [PtI(PEt$_3$)$_2$],[10] PPh$_2$–M {M = Mo(CO)$_5$, W(CO)$_5$ or Os$_3$(CO)$_{11}$}[11] and alkynyl/vinylidene-rhodium[12] and -ruthenium species[13] around the periphery of the organic ligand, in order (i) to probe the ability of the metal to participate in π delocalisation, (ii) investigate the potential for interaction of the metal d orbitals with the conjugated π orbitals of the organic moiety,[14] and (iii) provide precursors for the production of metal–aromatic polyyne networks. In general, there has been symmetric homosubstitution around the benzene core, but we have widened the scope to form a series of novel, *unsymmetrically* substituted triethynylbenzene complexes featuring ferrocenyl, ruthenium(II) and/or osmium(II) centres. The synthesis of these complexes is now detailed, along with spectroscopic characterisation and electrochemical studies to investigate electronic communication between the metal centres.

Results and discussion

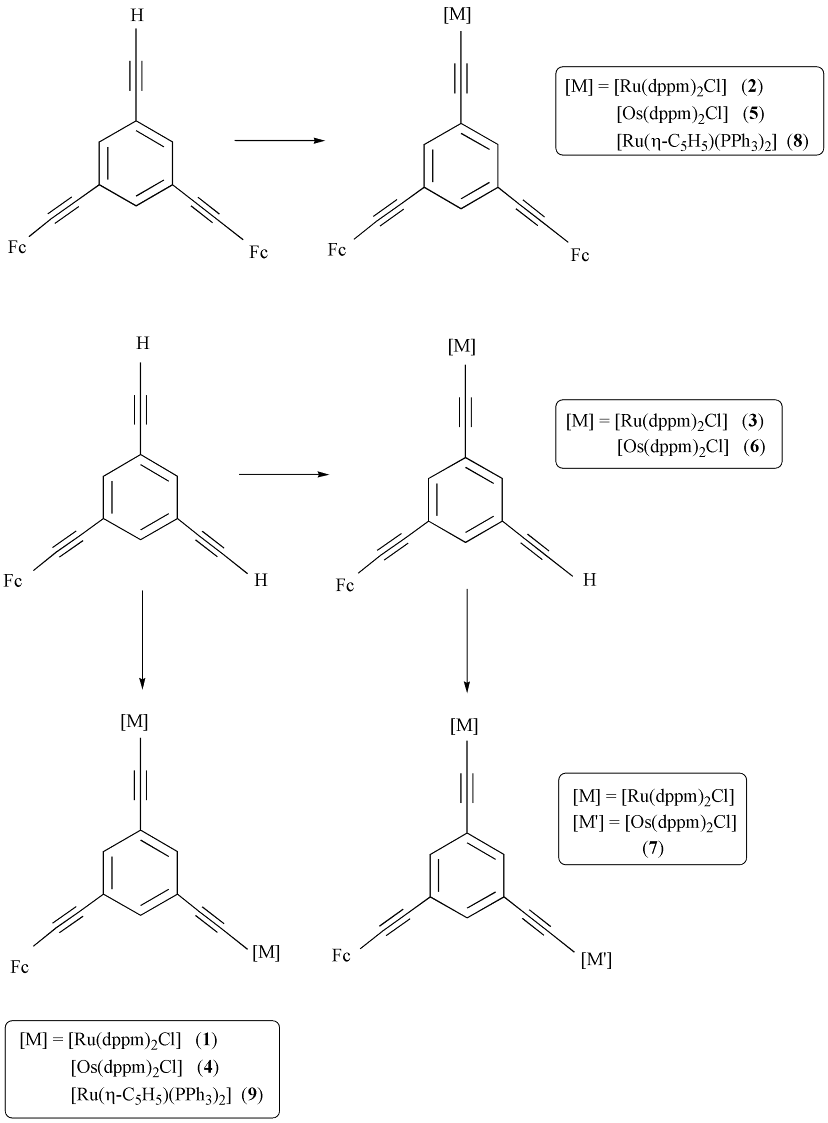
Synthesis and spectroscopic characterisation

The multinuclear σ-alkynyl complexes were of the type (XC$\equiv$C)$_3$C$_6$H$_3$ {X = H, C$_5$H$_5$FeC$_5$H$_4$, *trans*-[RuCl(dppm)$_2$], *trans*-[OsCl(dppm)$_2$] or [Ru(η-C$_5$H$_5$)(PPh$_3$)$_2$]} **1**–**9** (Scheme 1). It was most convenient to form initially the mono- and di-substituted ferrocenyl species[4] (as they are robust to further reactions), followed by addition of the metallic (Ru, Os) units. The yellow-orange microcrystalline products **1**–**9** were isolated in good to reasonable yields, depending on the synthetic method used. For the *trans*-[MCl(dppm)$_2$] complexes **1**–**7**, the preferred synthetic method was a modification of the one elucidated by Dixneuf and co-workers.[15] The reasonable yields obtained were a function of using fairly exact 1 : 1 or 1 : 2 stoichiometry of reactants, thereby reducing the number of possible by-products and side reactions. Complexes **8** and **9**, featuring the [Ru(η-C$_5$H$_5$)(PPh$_3$)$_2$] unit, were formed in good yields of *ca.* 70% using a mixture of KF, KPF$_6$, along with the requisite metal and ethynylbenzene starting reagents, in refluxing methanol–THF (and based on a method first pioneered by Lapinte and co-workers[5]). This approach is less selective and cannot efficiently be used to substitute in a stepwise fashion, as opposed to the 'Dixneuf' method. It is interesting that this stepwise substitution and the presence of one or two less sterically demanding ferrocenyl groups allows for full trisubstitution around the triethynylbenzene core. Previous attempts[4,16] to obtain the [{C$\equiv$CRu(dppm)$_2$Cl}$_3$C$_6$H$_3$] species had failed, presumably due to the steric bulk of the dppm groups. Uno and Dixneuf[13] have been able to introduce three {RuCl(dppe)$_2$} units around the core, but only after extending the 'arms' by incorporation of additional C$_6$H$_4$C$\equiv$C linkages.

Complexes **1**–**9** were characterised by microanalysis, IR and NMR spectroscopies and mass spectrometry. In the IR spectra the C$\equiv$C stretching values are diagnostic and represent a useful monitoring tool *i.e. ca.* 2215 cm^{-1} (FcC$\equiv$C), *ca.* 2065 (MC$\equiv$C) and *ca.* 2110 (HC$\equiv$C), along with the disappearance of the C$\equiv$*C–H* band (*ca.* 3300 cm^{-1}). It should be noted that the intensity of these ν(C$\equiv$C) signals can vary and in some of the systems not all of the expected bands are observed.

The ^{1}H NMR spectra (CDCl$_3$) of the complexes exhibit resonances characteristic of the CH$_2$ group in the bridging phosphine (δ 4.9), the alkynylic proton (when present) (δ 2.9), as well as a complicated series of multiplets for the aromatic

DOI: 10.1039/b005186l



Conditions for **1**, **2**, **3**, **7**: CH_2Cl_2, *cis*-[$RuCl_2(dppm)_2$], $NaPF_6$, N_2, r.t., 1, 8-diazabicyclo[5.4.0]undec-7-ene (dbu).
For **4**, **5**, **6**, **7**: CH_2Cl_2, *cis*-($OsCl_2(dppm)_2$], $NaPF_6$, N_2, r.t., dbu.
For **8**, **9**: Methanol, THF, [RuCl(η-C_5H_5)(PPh_3)$_2$], KF, KPF_6, N_2, heat.

Scheme 1 Synthesis of complexes **1**–**9**.

protons of the phenyls present (δ 7.0–7.6). In addition, the expected signals of the unsubstituted cyclopentadienyl rings are seen at δ 4.1–4.5, along with two 'pseudo' triplets for the non-equivalent protons on the substituted ring. The aromatic protons on the central benzene core warrant analysis. 1,3,5-Unsymmetrically substituted systems can have up to three different proton environments, but for a system with two identical substituents in the 1 and 3 positions and a different group in the 5 position, a triplet and doublet result from ^4J cross-ring coupling. For **1**–**9** this doublet consistently appears at higher field than the associated triplet, irrespective of the nature of the substitution, varying from δ 6.02 to 6.94. The triplet is not always observed as it is frequently obscured by the aromatic protons from the phosphine ligands on the metal centre. This is particularly so for the CpRu systems, as the resonances appear at lower frequency. The spectra for the osmium-substituted species exhibit broadening in most cases, being possibly due to the large osmium nucleus effectively 'pushing' the substituents together resulting in a slowly rotating 'cog-wheel' effect, causing fluxionality. This is further supported by the broadening of the dppm CH_2 protons in the same spectra, compared to that of the analogous ruthenium species. The ^{31}P-{^1H} NMR of **1**–**9** showed a singlet, indicative of equivalent phosphine environments (except **7**, which showed the expected two signals) and consistent with the *trans* geometry of the dppm ligands in **1**–**7** and the equivalent PPh_3 groups in **8** and **9**.

For each complex, mass spectrometry indicated the presence of a molecular ion, with characteristic isotope patterns from the metals; indeed, the metallic fragments (and loss of them) were often detected as major fragments.

X-Ray crystallography

The X-ray analysis of complex **2** shows the molecule to adopt a

Table 1 Selected bond lengths (Å) and angles (°) for complex **2**

Ru–C(8)	1.989(14)	Ru–Cl	2.490(3)
Ru–P(1)	2.352(3)	Ru–P(2)	2.339(4)
Ru–P(3)	2.318(3)	Ru–P(4)	2.354(3)
C(7)–C(8)	1.25(2)	C(9)–C(10)	1.20(2)
C(11)–C(12)	1.21(2)		
C(8)–Ru–P(3)	84.9(3)	C(8)–Ru–P(2)	95.1(3)
P(3)–Ru–P(2)	105.59(11)	C(8)–Ru–P(1)	91.5(3)
P(3)–Ru–P(1)	175.28(11)	P(2)–Ru–P(1)	71.57(11)
C(8)–Ru–P(4)	81.0(3)	P(3)–Ru–P(4)	70.85(11)
P(2)–Ru–P(4)	174.89(11)	P(1)–Ru–P(4)	111.71(11)
C(8)–Ru–Cl	172.4(3)	P(3)–Ru–Cl	102.07(11)
P(2)–Ru–Cl	85.99(11)	P(1)–Ru–Cl	81.65(11)
P(4)–Ru–Cl	98.28(11)	C(8)–C(7)–C(1)	176(2)
C(7)–C(8)–Ru	174.0(11)		

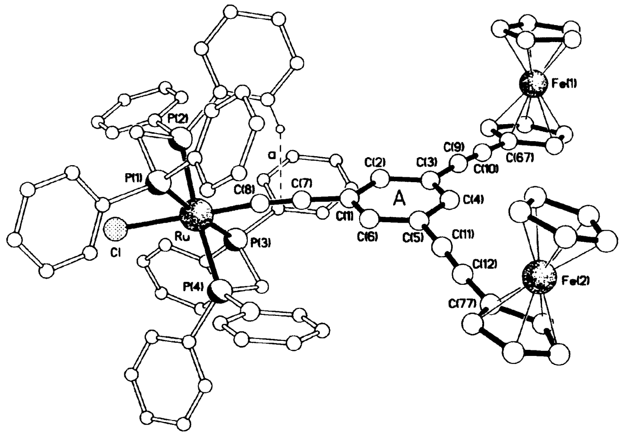


Fig. 1 The molecular structure of complex **2**, showing also the C–H···π interaction **a**; the H···π distance is 2.43 Å and the C–H···π angle 134°.

conformation in which the two ferrocenyl units are positioned on the same side of the 1,3,5-trisubstituted aromatic core (ring **A** in Fig. 1). All three ethynyl linkages are bent "down" out of the plane of ring **A** such that Ru, C(67) and C(77) lie 0.77, 0.46 and 0.57 Å out of the ring plane. In addition to these distortions, whereas the substituted cyclopentadienyl ring associated with C(67) is approximately coplanar with ring **A** (torsional twist about the ethynyl linkage of *ca.* 2°), that associated with C(77) is rotated out of this plane by *ca.* 21° about the ethynyl bond. In the Fe(1) ferrocenyl unit the two C_5 rings are staggered by *ca.* 12° with respect to each other, whilst in the Fe(2) unit the stagger is only *ca.* 2°. In both units the C_5 rings are essentially parallel, inclined by 2° for Fe(1) and 3° for Fe(2). The C≡C bonds in the ethynyl linkages to the two ferrocenyl units are fairly typical at 1.20(2) and 1.21(2) Å, whilst that linking to the ruthenium centre is slightly longer at 1.25(2) Å (Table 1). The Ru–C and Ru–Cl bond lengths [1.989(14) and 2.490(3) Å] do not differ significantly from those seen in, for example, *trans*-[Ru(dppe)$_2$Cl(C≡CPh)] and *trans*-[Ru(dppm)$_2${C≡C(C$_5$H$_4$FeC$_5$H$_5$)}$_2$],[17] though the C(7)–C(8) bond is somewhat longer (see above). The Ru–P distances are unexceptional. An interesting conformational feature of the molecule is the directing of one of the *ortho* hydrogen atoms of one of the phenyl rings attached to P(2) into the centre of the C(7)–C(8) ethynyl linkage; the H···π distance is short at 2.43 Å and clearly indicative of a significant interaction. There are no intermolecular packing interactions of note, possibly as a consequence of the inclusion of solvent acetone molecules.

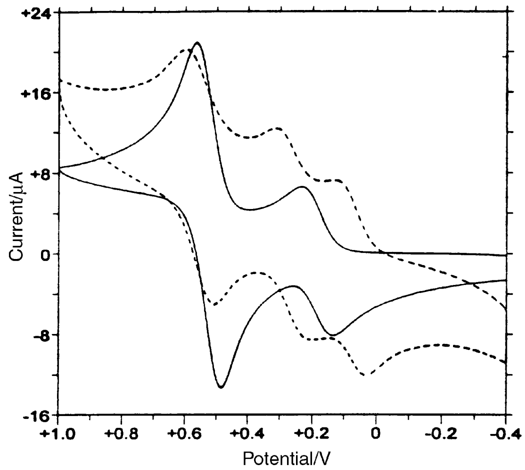


Fig. 2 Cyclic voltammetric responses recorded at a platinum electrode on CH_2Cl_2 solutions containing [NBu$_4$][PF$_6$] (0.2 mol dm^{-3}) and (——) complex **5** (0.7 × 10^{-3} mol dm^{-3}); (----) **4** (0.6 × 10^{-3} mol dm^{-3}). Scan rate 0.2 V s^{-1}.

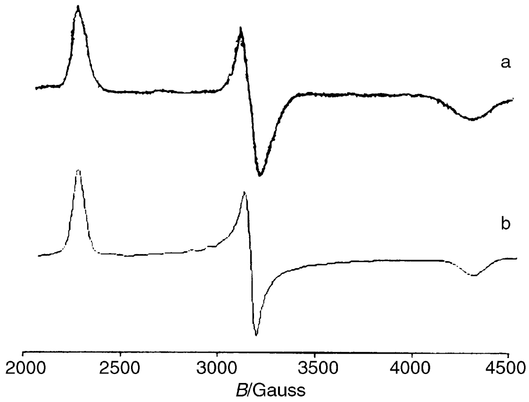


Fig. 3 Experimental (a) and simulated (b) X-band EPR spectra of the electrogenerated monocation [**5**]$^+$. T = 100 K.

Electrochemistry

Fig. 2 illustrates the cyclic voltammetric response given by the monoosmium complex **5** in dichloromethane solution, in comparison to that of the related diosmium complex **4**. Based on either the composition of **5** or the relative peak heights, it can be anticipated that the first step should be centred on the Os^{II}–Os^{III} redox change, whereas the second step should involve the concomitant oxidation of the two ferrocenyl subunits. In fact, controlled potential coulometry in connection with the first step (E_w = +0.3 V) consumes one electron per molecule. Attesting to the chemical reversibility of the oxidation process, the resulting solution displays a similar cyclic voltammetric profile to the original one. Despite the fact that as a consequence of the exhaustive one electron removal the original yellow solution assumes a green colour (λ_{max} = 710 nm) (which could be typical of ferrocenium species), in confirmation of the osmium-centred process, it becomes EPR active at liquid nitrogen temperatures (ferrocenium species are EPR active at *liquid helium* temperatures). For example, Fig. 3 shows the low temperature (T = 100 K) X-band EPR spectrum recorded on the electrogenerated monocation [**5**]$^+$.

The lineshape analysis can be carried out assuming an S = 1/2 Electron Spin Hamiltonian for the low-spin 5d^5 osmium(III) species.[18] The glassy signal displays a typical rhombic shape and is characterised by three well separated absorption peaks indicative of a very strong metal-ion character. The relevant g_i values (hereafter indicated as: g_l, g_m and g_h) depart significantly from the g electron value of 2.0023 and display a $\Delta g_{l-h} = g_l - g_h$ separation of about 1650 G. Such g_i values and the corresponding anisotropic ΔH_i reflect significant structural distortions of the osmium(III) octahedral co-ordination sphere. Furthermore, the second derivative glassy lineshape does not afford evidence either for osmium(III) hyperfine (hpf) satellite peaks [I(^{187}Os) = 1/2, I(^{189}Os) = 3/2; natural abundance ^{187}Os

Table 2 Formal electrode potentials (V, *vs.* SCE) and peak-to-peak separations (mV) for the oxidation processes exhibited by the complexes in CH_2Cl_2 solution

	$M^{II/III}$ oxidations				Fc oxidations				
Complex	$E^{o'}_{1st}$	ΔE_p[a]	$E^{o'}_{2nd}$	ΔE_p[a]	$E^{o'}_{1st}$	ΔE_p[a]	$E^{o'}_{2nd}$	ΔE_p[a]	Ref.
5	+0.19	90	—	—	+0.52	80	+0.52	80	[b]
4	+0.08	100	+0.27	100	+0.55	90	—	—	[b]
X = 'Os', X^2, X^3 = H	+0.19	84	—	—	—	—	—	—	[c]
X^1, X^2 = 'Os', X^3 = H	+0.05	59	+0.23	67	—	—	—	—	[c]
X^1 = Br, X^2, X^3 = Fc	—	—	—	—	+0.51	88	+0.51	88	[d]
X^1, X^2 = Br; X^3 = Fc	—	—	—	—	+0.54	81	—	—	[d]
2	+0.41	[e]	—	—	+0.52	80	+0.52	80	[b]
1	+0.30	60	+0.53	100	+0.53	100	—	—	[b]
X^1 = 'Ru', X^2 , X^3 = H	+0.41	81	—	—	—	—	—	—	[c]
X^1, X^2 = 'Ru', X^3 = H	+0.26	76	+0.46	76	—	—	—	—	[c]
8	+0.43	[e]	—	—	+0.53	[e]	+0.53	[e]	[b]
9	+0.34	[e]	+0.50	65	+0.50	65	—	—	[b]
X^1 = Ru*, X^2, X^3 = H	+0.48	[e]	—	—	—	—	—	—	[c]
X^1, X^2 = Ru*, X^3 = H	+0.32	[e]	+0.48	[e]	—	—	—	—	[c]
FcH	—	—	—	—	+0.39	87	—	—	[b]
FcC≡CH	—	—	—	—	+0.53	97	—	—	[d]

'Os' = $[Os(dppm)_2Cl]$. 'Ru' = $[Ru(dppm)_2Cl]$, Ru* = $[Ru(\eta\text{-}C_5H_5)(PPh_3)_2]$. [a] Measured at 0.2 V s^{-1}. [b] Present work. [c] From ref. 4(*b*). [d] From ref. 4(*a*). [e] Difficult to evaluate.

1.6%, ^{189}Os (16.1%)] or superhyperfine (shpf) interaction of the $S = 1/2$ unpaired electron with the four in-plane phosphorus nuclei $[I(^{31}P) = 1/2]$, due to effective anisotropic line broadening largely overlapping the corresponding (if any) hpf metal or shpf ligand couplings $[a_i(^{187}Os,\ ^{189}Os,\ ^{31}P) \leq \Delta H_i)$. As a consequence, the $5d^5$ metal atomic orbitals are expected to be mainly representative of the SOMO of the osmium(III) monocation.

The computed[19] EPR glassy parameters are: $g_l = 2.940(8)$, $g_m = 2.125(8)$, $g_h = 1.560(8)$, $\langle g\rangle = (g_l + g_m + g_h)/3 = 2.208(8)$, $\Delta H_l = 28.0(8)$, $\Delta H_m = 20.5(8)$, $\Delta H_h = 55.8(8)$ G. Upon raising the temperature, at the glassy–fluid transition phase the anisotropic signal drops out and the solution becomes EPR mute. Fast freezing of the fluid solution partially restores the original rhombic signal, indicating some chemical lability of the electrogenerated osmium(III) paramagnetic species under a non-inert atmosphere.

As Table 2 shows, the assignment of the first anodic step as Os^{II}-centred is consistent with the redox potentials of complexes $[(XC{\equiv}C)_3C_6H_3]$ {X^1 = $Os(dppm)_2Cl$, $X^2 = X^3$ = H; and X^1 = Br, $X^2 = X^3$ = Fc}, which can be considered as precursors of **5**. Finally, cyclic voltammetric tests on the solution resulting from exhaustive three-electron oxidation at $E_w = +0.8$ V show that some slow degradation affects the stability of the trication $[\mathbf{5}]^{3+}$. It is noteworthy that complex **4** exhibits three separate oxidation steps. Based on the redox behaviour of the precursors $[(XC{\equiv}C)_3C_6H_3]$ {$X^1 = X^2$ = $Os(dppm)_2Cl$; X^3 = H; $X^2 = X^3$ = Br, X^3 = Fc}, it can be deduced that the first two steps correspond to one-electron oxidation of the two osmium fragments, whereas the third involves oxidation of the ferrocenyl unit. Indeed, the peak height of the third step is somewhat higher than that of each of the two preceding steps. With consideration that the exhaustive electrolysis in connection with the third step leads to decomposition of the complex, an electrochemical step–chemical step–electrochemical step (ECE) process which partially generates FcC≡CH, which oxidises at essentially the same potential value as that of the third anodic process, cannot be ruled out.

It is clear that in complex **5** the two ferrocenyl units give rise to a single two-electron oxidation and do not electronically interact, whereas in **4** the two osmium units result in two separated one-electron oxidations and therefore do interact ($K_{com} = 1.6 \times 10^3$). These findings lend further support to our previous suggestion:[4b] the communication between metal fragments in polynuclear complexes is controlled by the nature of either the spacer(s) or the peripheral metal subunits.

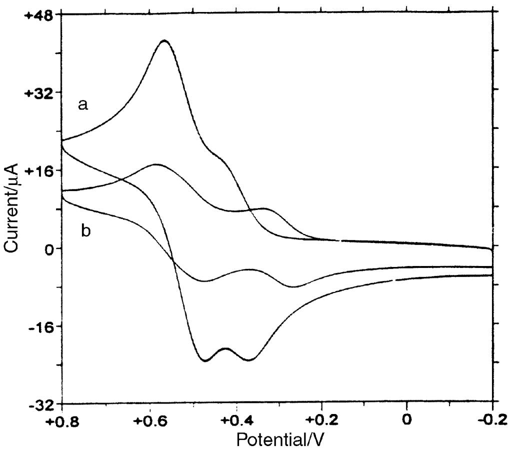


Fig. 4 Cyclic voltammetric responses recorded at a platinum electrode on CH_2Cl_2 solutions containing $[NBu_4][PF_6]$ (0.2 mol dm^{-3}) and: (a) complex **2** (0.8×10^{-3} mol dm^{-3}); (b) **1** (0.4×10^{-3} mol dm^{-3}). Scan rate 0.2 V s^{-1}.

As Fig. 4 shows, the ruthenium analogues **1** and **2** afford similar cyclic voltammetic responses to those of **4** and **5** but since the ruthenium subunits are more difficult to oxidise than the osmium congenors not only is the separation between the $Ru^{II/III}$ and $Fc^{0/+}$ steps in **2** lower than in **5**, but in the case of **1** the oxidation of the second ruthenium fragment becomes almost coincident with that of the ferrocenyl unit; even differential pulse voltammetry cannot succeed in separating the final $Ru^{II/III}/Fc^{0/+}$ steps. The same behaviour is essentially exhibited by the related ruthenium complexes **8** and **9**, and all relevant electrode potentials are listed in Table 2.

Experimental

All preparations were carried out using standard Schlenk techniques.[20] All solvents were distilled over standard drying agents under nitrogen directly before use and all reactions were carried out under an atmosphere of nitrogen. Alumina gel (neutral grade II) was used for chromatographic separations.

All NMR spectra were recorded using a Delta upgrade on a JEOL EX270 MHz spectrometer operating at 250.1 (^{1}H) and 101.3 MHz (^{31}P-{^{1}H}) respectively. Chemical shifts are reported in δ using $CDCl_3$ (^{1}H, δ 7.25) as the reference for ^{1}H spectra, while the ^{31}P-{^{1}H} spectra were referenced to H_3PO_4. Infrared spectra were recorded using NaCl solution cells (CH_2Cl_2)

on a Mattson Polaris Fourier Transform IR spectrometer, mass spectra using positive FAB methods on an Autospec Q mass spectrometer. Microanalyses were carried out by SACS, University of North London. Material and apparatus for electrochemistry and coupled EPR measurements have been described elsewhere.[21] All potential values are referred to the Saturated Calomel Electrode (SCE).

Synthesis

The complexes *cis*-[$Ru(dppm)_2Cl_2$], *cis*-[$Os(dppm)_2Cl_2$] and [$Ru(\eta\text{-}C_5H_5)(PPh_3)_2Cl$] were prepared by literature methods.[22,23] The complexes **1**–**9** were formed from the aforementioned species using the following general methods adapted from literature procedures.[5,15]

The following general method is relevant for the preparation of complexes **1**–**7**.

trans-[$(C_5H_5FeC_5H_4C\equiv C)C_6H_3\{C\equiv CRu(dppm)_2Cl\}_2$] 1. 1,3-Diethynyl-5-(ferrocenylethynyl)benzene (22 mg, 0.07 mmol), *cis*-[$RuCl_2(dppm)_2$] (125 mg, 0.13 mmol) and $NaPF_6$ (25 mg, 0.16 mmol) were suspended in CH_2Cl_2 (15 cm^3) and stirred overnight in the absence of light under N_2. The red solution was filtered to remove the excess of $NaPF_6$ and NaCl by-product and 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) (20 mg, 2 equivalents) was added. There was an immediate colour change and the yellow reaction mixture was stirred for 2 h. The solution was filtered and the solvent evaporated *in vacuo*. The residue was re-dissolved in a CH_2Cl_2–hexane mixture and, following slow solvent evaporation, complex **1** was isolated as a fine yellow powder which was washed with cold hexane (68 mg, 48%). mp 168–170 °C (decomp.) (Found: C, 68.13; H, 4.78. $C_{138}H_{100}Cl_2FeP_8Ru_2$ requires C, 68.38; H, 4.70%); $\tilde{\nu}$/cm^{-1} (CH_2Cl_2) 2212 ($C\equiv CFc$) and 2061 ($C\equiv CRu$); δ_H ($CDCl_3$) 7.46–7.00 (80 H, m, C_6H_5), 6.75 (1 H, t, C_6H_3), 6.56 (2 H, d, C_6H_3), 4.93 (8 H, m, PCH_2P), 4.55 (2 H, t, C_5H_4) and 4.28 (7 H, m, C_5H_4, C_5H_5); δ_P ($CDCl_3$) −5.73; *m*/*z* 2143 (M^+), 1239, 1126 and 870.

trans-[$(C_5H_5FeC_5H_4C\equiv C)_2C_6H_3\{C\equiv CRu(dppm)_2Cl\}$] 2. Yield 31 mg (42%). mp 174–176 °C (decomp.) (Found: C, 69.33; H, 4.58. $C_{82}H_{65}ClFe_2P_4Ru$ requires C, 69.24; H, 4.61%); $\tilde{\nu}$/cm^{-1} (CH_2Cl_2) 2214 ($C\equiv CFc$) and 2069 ($C\equiv CRu$); δ_H ($CDCl_3$) 7.35–7.12 (40 H, m, C_6H_5), 7.05 (1 H, t, C_6H_3), 6.05 (2 H, d, C_6H_3), 4.90 (4 H, t, PCH_2P), 4.52 (4 H, t, C_5H_4), 4.27 (10 H, s, C_5H_5) and 4.26 (4H, t, C_5H_4); δ_P ($CDCl_3$) −5.88; *m*/*z* 1422 (M^+), 1387, 1125 and 869.

trans-[$(C_5H_5FeC_5H_4C\equiv C)(HC\equiv C)C_6H_3\{C\equiv CRu(dppm)_2Cl\}$] 3. Yield 80 mg (42%). mp 162–166 °C (decomp.) (Found: C, 69.81; H, 4.71. $C_{72}H_{57}ClFeP_4Ru$ requires C, 69.83; H, 4.64%); $\tilde{\nu}$/cm^{-1} (CH_2Cl_2) 3284 ($C\equiv CH$), 2214 ($C\equiv CFc$) and 2065 ($C\equiv CRu$); δ_H ($CDCl_3$) 7.45–7.07 (20 H, m, C_6H_5), 7.12 (1 H, br t, C_6H_3), 6.04 (2 H, br m, C_6H_3), 4.90 (4 H, t, PCH_2P), 4.51 (2 H, t, C_5H_4), 4.25 (7 H, m, C_5H_4, C_5H_5) and 2.96 (1 H, s, $C\equiv CH$); δ_P ($CDCl_3$) −5.94; *m*/*z* 1237 (M^+) and 869.

trans-[$(C_5H_5FeC_5H_4C\equiv C)C_6H_3\{C\equiv COs(dppm)_2Cl\}_2$] 4. Yield 98 mg (46%). mp 190–192 °C (decomp.) (Found: C, 62.91; H, 4.32. $C_{122}H_{100}Cl_2FeOs_2P_8$ requires C, 63.13; H, 4.34%); $\tilde{\nu}$/cm^{-1} (CH_2Cl_2) 2215 ($C\equiv CFc$) and 2067 ($C\equiv COs$); δ_H ($CDCl_3$) 7.41–7.09 (83 H, m, C_6H_5, C_6H_3), 5.43 (4 H, m, PCH_2P), 4.51 (4 H, t, C_5H_4), 4.27 (10 H, s, C_5H_5) and 4.25 (4 H, t, C_5H_4); δ_P ($CDCl_3$) −48.47; *m*/*z* 2321 (M^+).

trans-[$(C_5H_5FeC_5H_4C\equiv C)_2C_6H_3\{C\equiv COs(dppm)_2Cl\}$] 5. Yield 135 mg (58%). mp 230–232 °C (decomp.) (Found: C, 65.44; H, 4.72. $C_{82}H_{65}ClFe_2OsP_4$ requires C, 65.15; H, 4.33%); $\tilde{\nu}$/cm^{-1} (CH_2Cl_2) 2215 ($C\equiv CFc$) and 2069 ($C\equiv COs$); δ_H ($CDCl_3$) 7.41–7.09 (40 H, m, C_6H_5), 7.03 (1 H, br m, C_6H_3), 6.05 (2 H, br d, C_6H_3), 5.43 (4 H, m, PCH_2P), 4.51 (4 H, t, C_5H_4), 4.27 (10 H, s, C_5H_5) and 4.23 (4 H, t, C_5H_4); δ_P ($CDCl_3$) −48.37; *m*/*z* 1513 (M^+), 1390, 1242, 1214, 959 and 756 (M^{++}).

trans-[$(C_5H_5FeC_5H_4C\equiv C)(HC\equiv C)C_6H_3\{C\equiv COs(dppm)_2Cl\}$] 6. Yield 53 mg (50%). mp 168–170 °C (decomp.) (Found: C, 65.01; H, 4.44. $C_{72}H_{57}ClFeOsP_4$ requires C, 65.14; H, 4.33%); $\tilde{\nu}$/cm^{-1} (CH_2Cl_2) 3301 ($C\equiv CH$), 2213 ($C\equiv CFc$) and 2067 ($C\equiv COs$); δ_H ($CDCl_3$) 7.40–7.00 (40 H, m, C_6H_5), 7.13 (1 H, t, C_6H_3), 6.02 (2 H, br m, C_6H_3), 5.43 (4 H, m, PCH_2P), 4.51 (2 H, t, C_5H_4), 4.25 (7 H, m, C_5H_4, C_5H_5) and 2.95 (1 H, s, $C\equiv CH$); δ_P ($CDCl_3$) −48.40; *m*/*z* 1328 (M^+), 1210, 1023 and 959.

trans-[$(C_5H_5FeC_5H_4C\equiv C)C_6H_3\{C\equiv CRu(dppm)_2Cl\}\{C\equiv COs(dppm)_2Cl\}$] 7. Yield 15 mg (50%). mp 134–136 °C (decomp.) (Found: C, 63.97; H, 4.30. $C_{122}H_{100}Cl_2FeOsP_8Ru$ requires C, 65.65; H, 4.52%); $\tilde{\nu}$/cm^{-1} (CH_2Cl_2) 2211 ($C\equiv CFc$) and 2065 ($C\equiv CM$); δ_H ($CDCl_3$) 7.48–6.98 (83 H, m, C_6H_5, C_6H_3), 5.45 (4 H, m, PCH_2POs), 4.93 (4 H, m, PCH_2PRu), 4.55 (2 H, t, C_5H_4), 4.30 (5 H, s, C_5H_5) and 4.27 (2 H, t, C_5H_4); δ_P ($CDCl_3$) −5.74 (Ru) and −48.41 (Os); *m*/*z* 2234 (M^+).

[$(C_5H_5FeC_5H_4C\equiv C)_2C_6H_3\{C\equiv CRu(\eta\text{-}C_5H_5)(PPh_3)_2\}$] 8. [$Ru(\eta\text{-}C_5H_5)(PPh_3)_2Cl$] (50 mg, 0.07 mmol, 1.2 equivalents), KF (4 mg, 1.2 equivalents), KPF_6 (13 mg, 1.2 equivalents) and **5** (34 mg, 0.06 mmol) were heated to reflux in methanol–THF (20 cm^3 : 2 cm^3) under N_2 for 24 h to give an orange-red suspension. The mixture was cooled to room temperature and filtered under N_2. The yellow-orange solid formed was washed with cold methanol (2 × 20 cm^3) and further purified by reprecipitation from a CH_2Cl_2–hexane two-layered system (48 mg, 69%). mp 236–238 °C (decomp.) (Found: C, 72.97; H, 4.63. $C_{73}H_{56}Fe_2P_2Ru\cdot CH_2Cl_2$ requires C, 73.12; H, 4.58%); $\tilde{\nu}$/cm^{-1} (CH_2Cl_2) 2217 ($C\equiv CFc$) and 2076 ($C\equiv CRu$); δ_H ($CDCl_3$) 7.45–7.10 (33 H, m, C_6H_5, C_6H_3), 4.50 (4 H, t, C_5H_4), 4.31 (5 H, t, C_5H_5) and 4.24–4.23 (14 H, m, C_5H_4, C_5H_5); δ_P ($CDCl_3$) 51.00; *m*/*z* 1209 (M^+), 691 and 590.

[$(C_5H_5FeC_5H_4C\equiv C)C_6H_3\{C\equiv CRu(\eta\text{-}C_5H_5)(PPh_3)_2\}_2$] 9. [$Ru(\eta\text{-}C_5H_5)(PPh_3)_2Cl$] (194 mg, 0.27 mmol, 2.4 equivalents), KF (16 mg, 2.4 equivalents), KPF_6 (49 mg, 2.4 equivalents) and complex **4** (53 mg, 0.11 mmol) were heated to reflux in methanol–THF (20 cm^3 : 2 cm^3) under N_2 for 24 h to give an orange suspension. The mixture was cooled to room temperature and filtered under N_2. The yellow-orange solid formed was washed with cold methanol (2 × 20 cm^3) and further purified by reprecipitation from a CH_2Cl_2–hexane two-layered system (131 mg, 70%). mp 214–216 °C (decomp.) (Found: C, 72.90; H, 5.02. $C_{104}H_{82}FeP_4Ru_2\cdot CH_2Cl_2$ requires C, 72.89; H, 4.82%); $\tilde{\nu}$/cm^{-1} (CH_2Cl_2) 2213 ($C\equiv CFc$) and 2065 ($C\equiv CRu$); δ_H ($CDCl_3$) 7.53–7.03 (61 H, m, C_6H_5, C_6H_3), 6.94 (2 H, d, C_6H_3) and 4.32–4.08 (19 H, m, C_5H_4, C_5H_5); δ_P ($CDCl_3$) 51.10; *m*/*z* 1714 (M^+).

Crystal data for complex 2

$C_{82}H_{62}ClFe_2P_4Ru\cdot 1.5Me_2CO$, $M = 1506.5$, monoclinic, space group $P2_1/c$ (no. 14), $a = 33.377(4)$, $b = 10.279(1)$, $c = 22.969(3)$ Å, $\beta = 109.63(1)°$, $V = 7422(2)$ Å^3, $Z = 4$, μ(Cu-Kα) = 62.3 cm^{-1}, $T = 183$ K, yellow plates, 0.23 × 0.17 × 0.03 mm, Siemens P4/RA diffractometer, graphite-monochromated Cu-Kα radiation, ω scans, 9878 independent reflections. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically using full matrix least squares based on F^2 to give $R1 = 0.098$, $wR2 = 0.246$ for 5844 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$]. The poor value of R is a consequence of the very thin nature and consequent partial warping of the crystals that resulted in both weak and diffuse diffraction peaks. Computations were carried out using the SHELXTL PC program system.[24]

CCDC reference number 186/2149.

See http://www.rsc.org/suppdata/dt/b0/b005186l/ for crystallographic files in .cif format.

Acknowledgements

We are very grateful to the EPSRC for funding a studentship (A. J. M.), the Royal Society for a small equipment grant and travel funds and Johnson Matthey plc for a loan of platinum salts. P. Zanello and F. Laschi gratefully acknowledge the financial support of the University of Siena.

References

1 U. H. F. Bunz, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 1073; F. Diederich and Y. Rubin, *Angew. Chem.*, *Int. Ed. Engl.*, 1992, **31**, 1101; T. Bartik, B. Bartik, M. Brady, R. Dembinski and J. A. Gladysz, *Angew. Chem.*, *Int. Ed. Engl.*, 1996, **35**, 414; U. H. F. Bunz, Y Rubin and Y. Tobe, *Chem. Soc. Rev.*, 1999, **28**, 107.

2 I. Manners, *Angew. Chem.*, *Int. Ed. Engl.*, 1996, **35**, 1602.

3 (*a*) N. Le Narvor, L. Toupet and C. Lapinte, *J. Am. Chem. Soc.*, 1995, **117**, 7129; (*b*) N. Le Narvor and C. Lapinte, *Organometallics*, 1995, **14**, 634; (*c*) P. J. Stang and R. Tykwinski, *J. Am. Chem. Soc.*, 1992, **114**, 4411; (*d*) W. Weng, T. Bartik and J. A. Gladysz, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 2199; (*e*) H. B. Fyfe, M. Mlekuz, D. Zaragarian, N. J. Taylor and T. B. Marder, *J. Chem. Soc.*, *Chem. Commun.*, 1991, 188; (*f*) M. S. Khan, D. J. Schwartz, N. A. Pasha, A. K. Kakkar, B. Lin, P. R. Raithby and J. Lewis, *Z. Anorg. Allg. Chem.*, 1992, **616**, 121; (*g*) M. Younus, A. Kohler, S. Cron, N. Chawdhury, M. R. A. Al-Mandhary, M. S. Khan, J. Lewis, N. J. Long, R. H. Friend and P. R. Raithby, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 3036; (*h*) M. C. B. Colbert, J. Lewis, N. J. Long, P. R. Raithby, M. Younus, A. J. P. White, D. J. Williams, N. N. Payne, L. Yellowlees, D. Beljonne, N. Chawdhury and R. H. Friend, *Organometallics*, 1998, **17**, 3034; (*i*) N. J Long, A. J. Martin, R. Vilar, A. J. P. White, D. J. Williams and M. Younus, *Organometallics*, 1999, **18**, 4261; (*j*) O. Lavastre, M. Even, P. H. Dixneuf, A. Pacreau and J.-P. Vairon, *Organometallics*, 1996, **15**, 1530; (*k*) I. R. Whittall, M. G. Humphrey, D. C. R. Hockless, B. W. Skelton and A. H. White, *Organometallics*, 1995, **14**, 3970; (*l*) T. P. Pollagi, T. C. Stoner, R. F. Dallinger, T. M. Gilbert and M. D. Hopkins, *J. Am. Chem. Soc.*, 1991, **113**, 703; (*m*) L. K. Myers, C. Langhoff and M. E. Thompson, *J. Am. Chem. Soc.*, 1992, **114**, 7560; (*n*) L. D. Field, A. V. George, D. C. R. Hockless, G. R. Purches and A. H. White, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 2011; (*o*) U. H. F. Bunz and V. Enkelmann, *Organometallics*, 1994, **13**, 3823; (*p*) E. Viola, C. Lo Sterzo and F. Trezzi, *Organometallics*, 1996, **21**, 4352; (*q*) M. I. Bruce, P. Hinterding, P. J. Low, B. W. Skelton and A. H. White, *Chem. Commun.*, 1996, 1009; (*r*) M. I. Bruce, J.-F. Halet, S. Kahal, P. J. Low, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1999, **578**, 155; (*s*) P. Nguyen, G. Lesley, T. B. Marder, I. Ledoux and J. Zyss, *Chem. Mater.*, 1997, **9**, 406; (*t*) S. L. James, M. Younus, P. R. Raithby and J. Lewis, *J. Organomet. Chem.*, 1997, **543**, 233.

4 (*a*) H. Fink, N. J. Long, A. J. Martin, G. Opromolla, A. J. P. White, D. J. Williams and P. Zanello, *Organometallics*, 1997, **16**, 2646; (*b*) N. J. Long, A. J. Martin, F. Fabrizi de Biani and P. Zanello, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 2017.

5 T. Weyland, C. Lapinte, G. Frapper, M. J. Cathorda, J.-F. Halet and L. Toupet, *Organometallics*, 1997, **16**, 2024; T. Weyland, K. Costuas, A. Mari, J.-F. Halet and C. Lapinte, *Organometallics*, 1998, **17**, 5569.

6 R. R. Tykwinski and P. J. Stang, *Organometallics*, 1994, **13**, 3203.

7 T. J. J. Muller and H. J. Lindner, *Chem. Ber.*, 1996, **129**, 607.

8 D. Tzalis and Y. Tor, *Chem. Commun.*, 1996, 1043.

9 M. J. Irwin, L. Manojlovic-Muir, K. W. Muir, R. J. Puddephatt and D. S. Yufit, *Chem. Commun.*, 1997, 219.

10 S. Leininger, P. J. Stang and S. Huang, *Organometallics*, 1998, **17**, 3981.

11 E. C. Constable, C. E. Housecroft, B. Krattinger, M. Neuberger, A. G. Schneider and M. Zehnder, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 2427; E. C. Constable, C. E. Housecroft, B. Krattinger, M. Neuberger and M. Zehnder, *Organometallics*, 1999, **18**, 2565.

12 H. Werner, P. Bachmann, M. Laubender and O. Gevert, *Eur. J. Inorg. Chem.*, 1998, 1217.

13 M. Uno and P. H. Dixneuf, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 1714.

14 D. Astruc, *Electron Transfer and Radical Processes in Transition Metal Chemistry*, VCH, New York, 1995.

15 D. Touchard, P. Haquette, N. Pirio, L. Toupet and P. H. Dixneuf, *Organometallics*, 1993, **12**, 3132; D. Touchard, P. Haquette, S. Guesmi, L. Le Pichon, A. Daridor, L. Toupet and P. H. Dixneuf, *Organometallics*, 1997, **16**, 3640.

16 I. R. Whitall, M. G. Humphrey, S. Houbrechts, J. Maes, A. Persoons, S. Schmid and D. C. R. Hockless, *J. Organomet. Chem.*, 1997, **544**, 277.

17 C. W. Faulkner, S. L. Ingham, M. S. Khan, J. Lewis, N. J. Long and P. R. Raithby, *J. Organomet. Chem.*, 1994, **487**, 139; M. C. B. Colbert, J. Lewis, N. J. Long, P. R. Raithby, A. J. P. White and D. J. Williams, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 99.

18 F. E. Mabbs and D. Collison, in *Electron Paramagnetic Resonance of d Transition Metal Compounds*, *Studies in Inorganic Chemistry*, Elsevier, New York, 1992, vol. 16.

19 J. P. Lozos, B. M. Hoffman and C. G. Franz, *QCPE*, 1974, 259.

20 R. J. Errington, *Advanced Practical Inorganic and Metalorganic Chemistry*, Blackie, London, 1997.

21 P. Zanello, F. Laschi, M. Fontani, C. Mealli, A. Ienco, K. Tang, X. Jin and L. Li, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 965.

22 J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1961, 896.

23 M. I. Bruce and N. J. Windsor, *Aust. J. Chem.*, 1997, **30**, 1601; M. I. Bruce, C. Hameister, A. G. Swincer and R. C. Wallis, *Inorg. Synth.*, 1982, **21**, 76.

24 SHELXTL PC, version 5.03, Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1994.