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Synthetic, spectroscopic and electrochemical characterisation of mixed-metal acetylide complexes

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Abstract

Terminal metal acetylide complexes *trans*-[$(dppm)_2(Cl)Os(-C{\equiv}C\text{-R-}C{\equiv}C-H)$] (dppm = $Ph_2PCH_2PPh_2$, R = -*p*-C_6H_4– (**1**), -*p*-C_6H_4–C_6H_4-*p*- (**2**)) and *trans*-[$(Et_3P)_2(Ph)Pt(C{\equiv}C$-*p*-$C_6H_4-C{\equiv}CH)$] (**3**) have been synthesised by the application of established synthetic routes. Acetylide bridged mixed-metal complexes *trans*-[$(dppm)_2(Cl)Os-C{\equiv}C$-*p*-$C_6H_4-C{\equiv}C-Ru(Cl)(dppm)_2$] (**4**), *trans*-[$(Et_3P)_2(Ph)Pt-C{\equiv}C$-*p*-$C_6H_4-C{\equiv}C-Ru(Cl)(dppm)_2$] (**5**), *trans*-[$(Et_3P)_2(Ph)Pt-C{\equiv}C$-*p*-$C_6H_4-C{\equiv}C-Ru(Ph_3P)_2(\eta^5\text{-}C_5H_5)$] (**6**) and *trans*-[$(Et_3P)_2(Ph)Pt-C{\equiv}C$-*p*-$C_6H_4-C{\equiv}C-Ru(Ph_3P)_2(\eta^5\text{-}C_5H_4-CH_3)$] (**7**) have been formed by the reaction of **1**, **2** and **3** with the appropriate metal chlorides. Complex **6** is less soluble in common organic solvents than the other complexes but this insolubility has been overcome by introducing a methylcyclopentadienyl group on the ruthenium centre to form complex **7**. Complexes **1**, **2**, **4**, **6** and **7** have shown reversible redox chemistry and in the di-metallic complexes, intramolecular electronic communication has been investigated by cyclic voltammetry. The shift in the lowest energy band in the UV–vis spectra of the mixed-metal complexes **4**, **5**, **6** and **7** is largely dependent on the various metal fragments. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Acetylide; Ruthenium; Osmium; Platinum; Electrochemistry

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1. Introduction

There is a growing interest in the chemical, physical and material properties of organometallic dimers, oligomers and polymers in which a conjugated carbon framework is spanned by transition metal centres [1–9]. Transition metal centres possess redox, magnetic, optical and electronic properties and by changing the ligand in a complex or polymer, variation in these properties can be ‘fine-tuned’ and optimised [10–15]. The conjugated acetylide units in metal poly-yne systems, which formally have alternate triple and single bonds, have a rigid-rod geometry and can act as good potential pathways for electronic interaction between metal centres. It has been shown that the electronic and optical properties of these metal poly-ynes can be varied by changing the nature of the spacer groups of an acetylide bridge [16,17] and in metal poly-ynes, π-electron delocalisation can be transferred through the metals utilising their diffuse d-orbitals [18,19]. The chemical and physical properties of carbon-rich organic polymers often cannot be exploited due to their poor solubility but this can be improved by incorporating alkyl substitutents on the ligands [20].

The electronic communication (metal–metal interaction) between metal centres of dimetallic complexes and polymers can be investigated by electrochemical studies, where the metal centres are redox active [21,22]. Acetylide-bridged homo-metallic systems of the type $M-C{\equiv}C-R-C{\equiv}C-M$ (M = Fe and Ru; R = aromatic or heteroaromatic spacer) and Fc–C≡C–C_6H_4-*p*-C≡C–M (Fc = ferrocenyl, M = Ru, Os and Mn) have been studied extensively by our group and by others [21–25].

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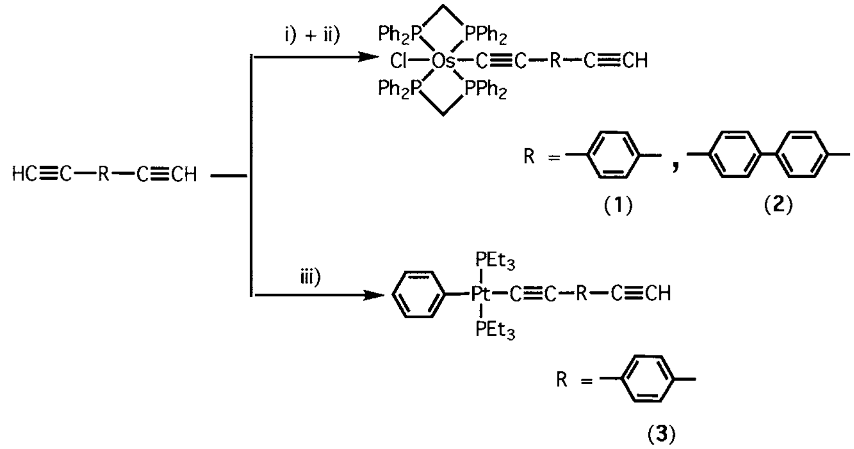


Scheme 1. Synthesis of terminal acetylide complexes. Reagents and conditions: i) *cis*-[(dppm)$_2$OsCl$_2$], 2NaPF$_6$, CH$_2$Cl$_2$; ii) DBU; iii) *trans*-[(Et$_3$P)$_2$Pt(Ph)Cl], CuI, Et$_2$NH.

Compared to homometallic systems however, literature reports on mixed metal acetylide systems are very rare [26]. We have considered the possibility of improving electronic communication in systems where the acetylide bridge links alternate donor and acceptor metal centres in a polymeric chain. We therefore, report herein the design and synthesis of osmium and platinum di-yne precursors and their mixed-metal complexes of ruthenium. Electrochemical studies of these complexes are performed to elucidate the metal–metal interactions and the UV–vis spectra of the complexes show how the metals and ligands influence the lowest energy band in the mixed-metal complexes.

2. Results and discussion

2.1. Synthesis of terminal metal acetylide complexes

The complexes *trans*-[(dppm)$_2$(Cl)Os(C≡C-*p*-C$_6$H$_4$–C≡C–H)] (**1**) and *trans*-[(dppm)$_2$(Cl)Os(C≡C-*p*-C$_6$H$_4$–C$_6$H$_4$-*p*-C≡C–H)] (**2**) were prepared by a modification of published procedures [26,27]. The reaction of *cis*-[(dppm)$_2$OsCl$_2$] with one equivalent of terminal di-acetylenes H–C≡C-R-C≡C–H (R = *p*-C$_6$H$_4$, *p*-C$_6$H$_4$–C$_6$H$_4$-*p*-) and two equivalents of NaPF$_6$ gave vinylidene complexes which were not isolated but instead, deprotonated in situ using one equivalent of DBU (Scheme 1).

Complexes **1** and **2** were characterised by IR, ^{1}H-NMR, ^{31}P-{^{1}H}-NMR and mass spectroscopies. Characteristic ν(C≡C) and ν(≡C–H) vibrations were observed in the IR spectrum at 2071 and ca. 3300 cm^{-1}, respectively. Terminal acetylenic protons of the complexes appeared at ca. 3.05 ppm as a singlet and the protons of the aromatic spacer groups displayed the expected (AB)$_2$ pattern in the ^{1}H-NMR spectra of the complexes. The ^{31}P-{^{1}H}-NMR spectra contain singlets at − 190 ppm which are consistent with the symmetrical *trans* orientation of the ligands and the + FAB mass spectra of the complexes exhibit peaks corresponding to the molecular ion.

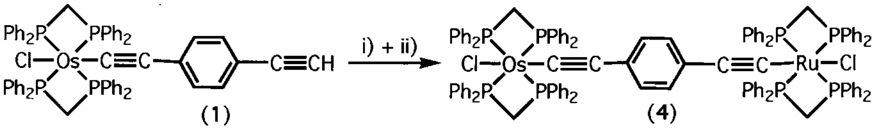
The platinum di-yne *trans*-[(Et$_3$P)$_2$(Ph)Pt(C≡C-*p*-C$_6$H$_4$–C≡CH)] (**3**) was prepared by applying the synthetic route of Sonogashira et al. [28]. The reaction of *trans*-[(Et$_3$P)$_2$(Ph)PtCl] with two equivalents of HC≡C-*p*-C$_6$H$_4$–C≡CH, in CH$_2$Cl$_2$/Et$_2$NH in the presence of CuI, while stirring at room temperature (r.t.) for 4 h, afforded complex **3** as an off white solid in an 83% yield (Scheme 1).

The IR spectrum of **3** displays characteristic ν(C≡C) and ν(≡C–H) frequencies at 2091 and 3295 cm^{-1} which lie in the usual frequency ranges for platinum σ-acetylide complexes [28]. The terminal acetylenic proton C≡C–**H** of the complex appears at 3.08 ppm as a singlet in the ^{1}H-NMR spectrum and the ^{31}P-{^{1}H}-NMR spectrum contains a singlet with Pt satellites (coupling constant $^1J_{(\mathrm{Pt-P})}$ of 2679 Hz) which is consistent with the *trans* geometry of the phosphine ligands. The + FAB mass spectrum displays a signal for the molecular ion of **3** at 633 a.m.u. and shows the loss of the acetylide ligand.

2.2. Synthesis of mixed-metal acetylide complexes

The reaction of *cis*-[(dppm)$_2$RuCl$_2$] with one equivalent of *trans*-[(dppm)$_2$(Cl)Os(C≡C-*p*-C$_6$H$_4$–C≡C–H)] **1** and two equivalents of NaPF$_6$, gave a vinylidene complex which upon in situ deprotonation by DBU afforded *trans*-[(dppm)$_2$(Cl)Os(C≡C-*p*-C$_6$H$_4$–C≡C–Ru-(Cl)(dppm)$_2$] (**4**) in a 45% yield (Scheme 2).

The IR spectrum of the complex contains a characteristic broad peak at 2075 cm^{-1} corresponding to a ν(C≡C) stretching frequency. The mono-terminal acetylides of ruthenium and osmium have a ν(C≡C) stretching frequency in the same region (2070 cm^{-1}) [29], therefore, the broad peak at 2075 cm^{-1} is probably due to both ruthenium and osmium bound acetylide



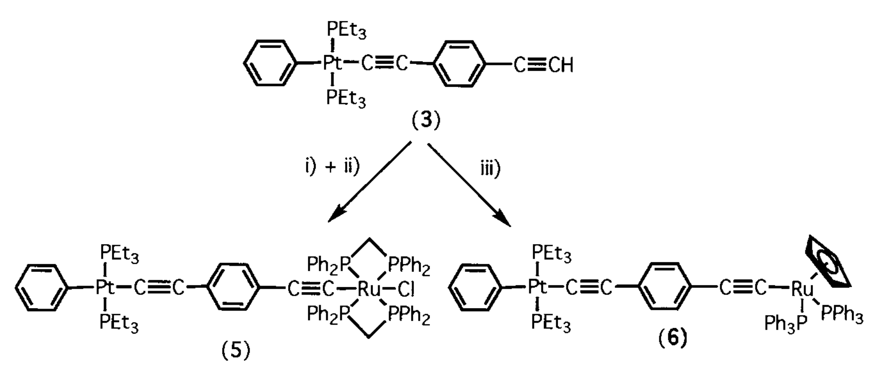
Scheme 2. Synthesis of Os–Ru mixed-metal acetylide complexes. Reagents and conditions: i) *cis*-[(dppm)$_2$RuCl$_2$], 2NaPF$_6$, CH$_2$Cl$_2$, ii) DBU.

links. The ^{31}P-{^{1}H}-NMR spectrum of the complex contains two signals at −147.5 and −190.2 ppm corresponding to the ruthenium and osmium bound phosphorus atoms, respectively and multiplets at 4.90 and 5.44 ppm in the ^{1}H-NMR spectrum correspond to the PC**H**$_2$P protons of the dppm ligands at ruthenium and osmium centres, respectively. The +FAB mass spectrum displays a signal at 2022 corresponding to the molecular ion of the complex **4**.

The complex *trans*-[(Et$_3$P)$_2$(Ph)Pt–C≡C-*p*-C$_6$H$_4$–C≡C–Ru(Cl)(dppm)$_2$] (**5**) was synthesised and purified following the method discussed for **4** and obtained in an 85% yield (Scheme 3). All the spectroscopic data are in accord with the formulation of the new complex. The IR spectrum shows two ν(C≡C) frequencies at 2075 and 2091 cm^{-1} which are consistent with the frequencies of ruthenium and platinum bound σ-acetylides, respectively [27]. The ^{31}P-{^{1}H}-NMR spectrum of **5** contains a singlet at −147.5 ppm corresponding to the *trans* geometry of the ligands which is a common feature of ruthenium mono-chloro-acetylides [27,29] and a signal at −131.4 ppm with Pt satellites ($^1J_{(\mathrm{Pt-P})}$ = 2688) corresponding to **P**Et$_3$ coordinated to the platinum centre. The +FAB mass spectrum of complex **5** shows a molecular ion signal at 1537 a.m.u. The ^{31}P-{^{1}H}-NMR and mass spectra also show the formation of trace amounts of the trinuclear platinum and ruthenium complex *trans*-[(Et$_3$P)$_2$(Ph)Pt–C≡C-*p*-C$_6$H$_4$–C≡C–Ru(dppm)$_2$–C≡C-*p*-C$_6$H$_4$–C≡C–Pt(Ph)(PEt$_3$)$_2$] which was formed by the substitution of two chlorides of [Ru(dppm)$_2$Cl$_2$] (subsequent efforts to form this trinuclear complex have been unsuccessful to date). To alleviate the formation of mixures, the ruthenium-mono-chloride precursor [(η^5-C$_5$H$_5$)(Ph$_3$P)$_2$RuCl] was used in the synthesis of the mixed metal di-yne *trans*-[(Et$_3$P)$_2$(Ph)Pt–C≡C-*p*-C$_6$H$_4$–C≡C–Ru(Ph$_3$P)$_2$(η^5-C$_5$H$_5$)] (**6**). The synthetic route applied here is analogous to that previously reported for the preparation of ruthenium bis-acetylides [30]. Complex **6** was obtained by refluxing a suspension of [(η^5-C$_5$H$_5$)(Ph$_3$P)$_2$RuCl] and *trans*-[(Et$_3$P)$_2$(Ph)Pt–C≡C-*p*-C$_6$H$_4$–C≡CH)] (**3**), in methanol for 0.5 h, followed by treatment with a 10-fold excess of sodium in the reaction mixture after cooling. The product was obtained as a pale yellow powder in a 49% yield (Scheme 3) but is less soluble in common organic solvents than the other complexes and also decomposes gradually in chlorinated solvents. To overcome the solubility problems, a similar methyl-substituted cyclopentadienyl complex *trans*-[(Et$_3$P)$_2$(Ph)Pt–C≡C-*p*-C$_6$H$_4$–C≡C–Ru(Ph$_3$P)$_2$(η^5-C$_5$H$_4$–CH$_3$)] (**7**) was synthesised, using the same procedure. Complex **7**, with the solubilising methylcyclopentadienyl group is significantly more soluble and fairly stable in chlorinated solvents.

The IR spectra of **6** exhibited two ν(C≡C) stretching frequencies at 2070 and 2090 cm^{-1} for the σ-bonded ruthenium and platinum acetylides, respectively. The five protons of the η^5-bound C$_5$**H**$_5$ group appeared at 4.47 ppm as a singlet in the ^{1}H-NMR spectrum of the complex and the ^{31}P-{^{1}H}-NMR spectrum of the complex displayed a singlet at −89.9 ppm which was assigned to the **P**Ph$_3$ bonded to ruthenium and another singlet at −130.1 with Pt satellites ($^1J_{(\mathrm{Pt-P})}$ = 2695 Hz) was assigned to **P**Et$_3$ bonded to platinum. The mass spectrum contained a signal at 1325 a.m.u. corresponding to the molecular ion peak of complex **6**. Complex **7** was also characterised similarly (spectroscopic data in Section 4.2.6).

Table 1 shows the lowest absorption bands of all the mono- and di-nuclear complexes. Molecular orbital cal-



Scheme 3. Synthesis of Pt–Ru mixed metal acetylide complexes. Reagents and conditions: i) *cis*-[(dppm)$_2$RuCl$_2$], 2NaPF$_6$, CH$_2$Cl$_2$, ii) DBU; iii) [Ru(C$_5$H$_5$) (PPh$_3$)$_2$Cl], Na, CH$_3$OH.

Table 1
Electrode potentials and lowest energy absorption peaks of mononuclear and mixed-metal acetylide complexes

Complex	$E_{\frac{1}{2}\text{I}}$ (V)	$E_{\frac{1}{2}\text{II}}$ (V)	$\lambda_{\max}$ in nm (log ε)
Trans-[(dppm)$_2$(Cl)Os(–C≡C-*p*-C$_6$H$_4$–C≡C–H)] **1**	−0.16	—	359 (4.30)
Trans-[(dppm)$_2$(Cl)Os–C≡C-*p*-C$_6$H$_4$–C$_6$H$_4$-*p*-C≡C–H)] **2**	−0.26	—	381 (4.11)
Trans-[(dppm)$_2$(Cl)Ru(–C≡C-*p*-C$_6$H$_4$–C≡C–H)] [27]	0.0	—	386 (4.35)
Trans-[(Et$_3$P)$_2$(Ph)Pt–C≡C-*p*-C$_6$H$_4$–C≡C–H) **3**	—	—	327 (4.58)
Trans-[(dppm)$_2$(Cl)Os–C≡C-*p*-C$_6$H$_4$–C≡C–Ru(Cl)(dppm)$_2$] **4**	−0.12	−0.48	380 (4.11)
Trans-[(Et$_3$P)$_2$(Ph)Pt–C≡C-*p*-C$_6$H$_4$–C≡C–Ru(Cl)(dppm)$_2$] **5**	0.07[b]	—	360 (4.69)
[(η^5-C$_5$H$_5$)(Ph$_3$P)$_2$RuCl]	+0.12	—	—
[(η^5-C$_5$H$_5$)(Ph$_3$P)$_2$Ru(C≡C–C$_6$H$_5$)] [33][c]	0.0	—	306 (4.60)
Trans-[(Et$_3$P)$_2$(Ph)Pt–C≡C-*p*-C$_6$H$_4$–C≡C–Ru(Ph$_3$P)$_2$(η^5-C$_5$H$_5$)] **6**	−0.13	—	360 (4.67)
Trans-[(Et$_3$P)$_2$(Ph)Pt–C≡C-*p*-C$_6$H$_4$–C≡C–Ru(Ph$_3$P)$_2$(η^5-C$_5$H$_4$–CH$_3$)] **7**	−0.19	—	360 (4.46)

[a] Scan rate 100 mV s^{-1}. All $E_{\frac{1}{2}}$ values referenced to ferrocene in the same system. [b] Irreversible anodic peak. [c] Fc = 0.55 V versus Ag/AgCl.

culations on the Group 10 acetylide systems *trans*-[L$_2$M(C≡CR)$_2$] (L = alkyl phosphines; M = Pt, Pd, Ni; R = H, alkyl, aryl) reveal that the lowest energy bands arise from the electronic transitions from π(C≡CR) to π(C≡CR)* orbitals. These transitions possess charge-transfer character as a result of mixing between the (C≡CR)* and metal p-orbitals [31]. Our previously reported molecular orbital calculations on Group 8 acetylide systems [L$_4$M(C≡C-*p*-C$_6$H$_4$–C≡CH)$_2$] (L = phosphine, CO; M = Fe, Ru) shows that the highest occupied molecular orbitals (HOMO) are d-like and the lowest unoccupied molecular orbitals (LUMO) are C≡C*-like in character [32]. Based on these previous studies we can assign the lowest energy band in the spectra due to the platinum complexes as being a result of ligand to metal charge transfer (LMCT) and that of ruthenium and osmium species as being due to the metal to ligand charge transfer (MLCT) transitions. Indeed, Whittall et al. assigned the lowest energy band of [(η^5-C$_5$H$_5$)Ru(PPh$_3$)$_2$(C≡C–R)] (R = Ph, C$_6$H$_4$-*p*-NO$_2$) as a MLCT band [33]. The lowest energy band of the dinuclear ruthenium–osmium complex (**4**) and ruthenium–platinum complex (**5**) lies in between their mononuclear precursors (Fig. 1). No significant shifts were observed in the lowest energy bands of complexes **6** and **7** compared to **5** when ligand environments were changed around ruthenium.

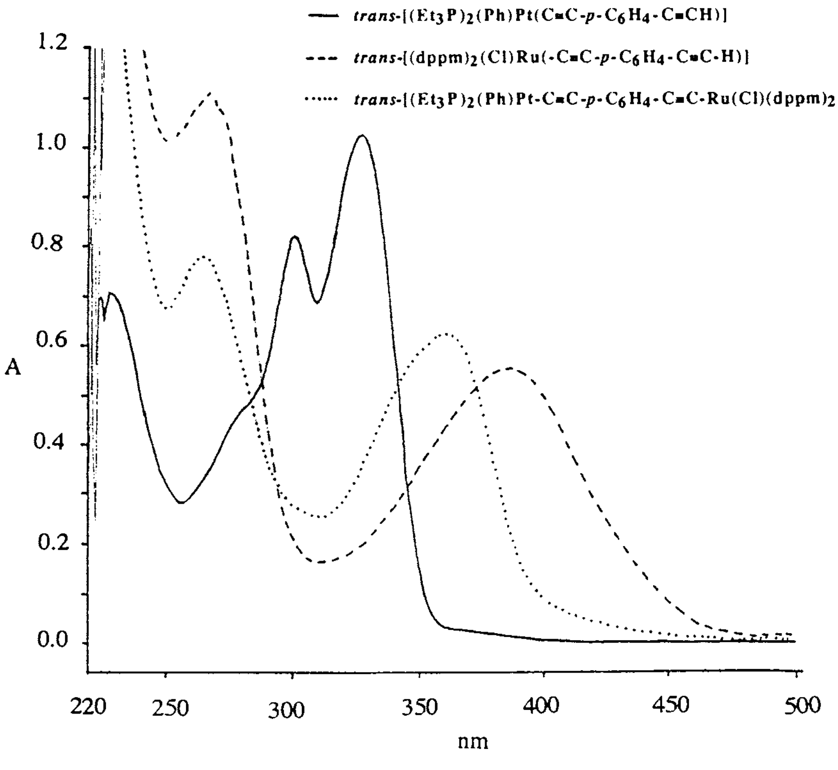


Fig. 1. UV–vis spectra of platinum and ruthenium mononuclear and mixed metal acetylide complexes.

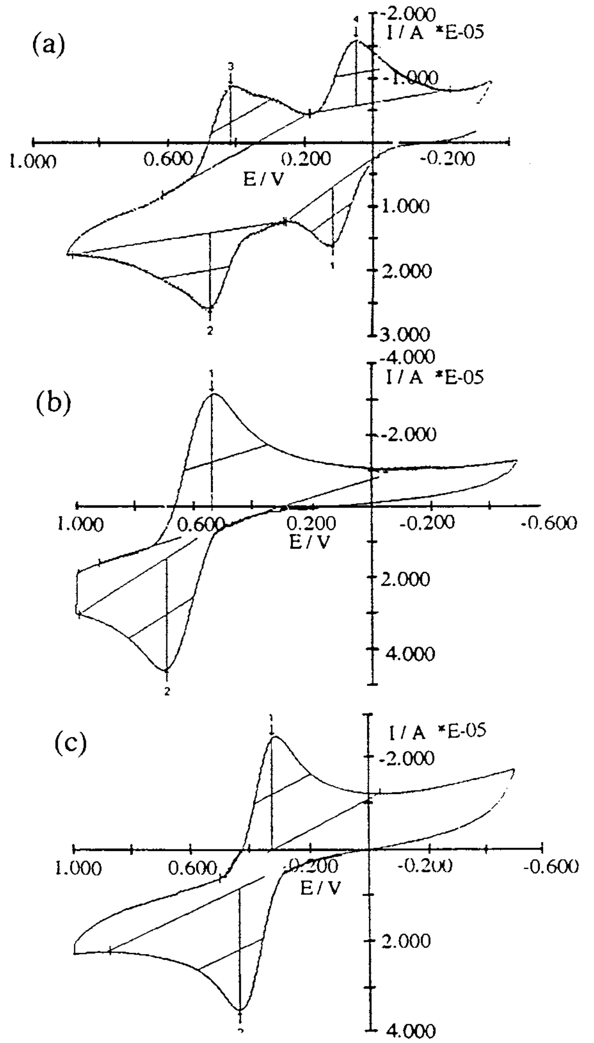


Fig. 2. Cyclic voltammograms of (a) *trans*-[$(dppm)_2(Cl)Ru{-}C{\equiv}C$-*p*-$C_6H_4{-}C{\equiv}C{-}Os(Cl)(dppm)_2$] (b) *trans*-[$(dppm)_2(Cl)Ru({-}C{\equiv}C$-*p*-$C_6H_4{-}C{\equiv}C{-}H)$] (c) *trans*-[$(dppm)_2(Cl)Os({-}C{\equiv}C$-*p*-$C_6H_4{-}C{\equiv}C{-}H)$].

3. Electrochemistry of mixed-metal acetylide complexes

The cyclic voltammogram of the complex *trans*-[$(dppm)_2(Cl)Os{-}C{\equiv}C$-*p*-$C_6H_4{-}C{\equiv}C{-}Ru(Cl)(dppm)_2$] (**4**) displays two well-separated ($\Delta E_{\frac{1}{2}} = 0.36$ V) reversible waves ($\Delta E_1 = 63$ eV, $\Delta E_2 = 58$ eV) at −0.48 and −0.12 V which can be considered as two one electron oxidations at the osmium and ruthenium centres, respectively (Fig. 2). The reference complexes *trans*-[$(dppm)_2(Cl)Ru(C{\equiv}C$-*p*-$C_6H_4{-}C{\equiv}C{-}H)$] [27] and *trans*-[$(dppm)_2(Cl)Os(C{\equiv}C$-*p*-$C_6H_4{-}C{\equiv}C{-}H)$] (**1**) are reversibly oxidised at 0.0 and −0.16 V, respectively (Fig. 2). From the cyclic voltammogram of **4**, it may be concluded that the ruthenium centre releases electron density to the osmium unit via the $C{\equiv}C$-*p*-$C_6H_4{-}C{\equiv}C$ bridge and thus the electrode potential of the Os^{II}/Os^{III} couple is lowered significantly (from −0.16 to −0.48 V). Conversely, the Ru^{II} centre undergoes oxidation at −0.12 V which was unexpected, as the oxidation of the ruthenium centre should be more difficult after the oxidation of the osmium centre.

$$Os^{II}Ru^{II} \underset{+e}{\overset{-e}{\rightleftharpoons}} Os^{III}Ru^{II} \underset{+e}{\overset{-e}{\rightleftharpoons}} Os^{III}Ru^{III}$$

Electrochemical investigations of dimetallic complexes of the type *trans*-[$(dppm)_2(Cl)M{-}C{\equiv}C$-*p*-$C_6H_4{-}C{\equiv}C{-}M(dppm)_2(Cl)$] (M = Ru and Os) have shown a similar trend in that the ruthenium centres oxidised at −0.30 and 0.0 V and the osmium centres oxidised at −0.51 and −0.21 V, respectively [25]. Theoretical studies are underway to try and rationalise these observations, but it is likely that this anomalies arise from the formation of a delocalised allenylidene type structure facilitating unusual electrochemical behaviour. For **5** an irreversible wave was observed at 0.07 V, which may be due to the oxidation of the ruthenium centre. The previously reported trinuclear mixed metal complex *trans*-[$(dppe)_2(Cl)Ru{-}C{\equiv}C$-*p*-$C_6H_4{-}C{\equiv}C{-}(Bu_3P)_2Pd{-}C{\equiv}C$-*p*-$C_6H_4{-}C{\equiv}C{-}Ru(Cl)(dppe)_2$] showed a reversible wave at 0.33 V versus SCE and an irreversible wave at 1.14 versus SCE which were due to the oxidations of Ru^{II}/Ru^{III} and Ru^{III}/Ru^{IV}, respectively [26]. The cyclic voltammogram of the mixed-metal di-yne *trans*-[$(Et_3P)_2(Ph)Pt{-}C{\equiv}C{-}C_6H_4$-*p*-$C{\equiv}C{-}Ru(Ph_3P)_2(\eta^5\text{-}C_5H_5)$] (**6**) showed a quasi-reversible oxidation ($\Delta E = 86$ mV) wave at −0.13 V which is significantly lower than the oxidation potential of [$(Ph_3P)_2(\eta^5\text{-}C_5H_5)RuCl$] ($E_{\frac{1}{2}} = +0.12$ V) and [$(Ph_3P)_2(\eta^5\text{-}C_5H_5)Ru(C{\equiv}C{-}C_6H_5)$] ($E_{\frac{1}{2}} = 0.0$ V) [33], thus indicating that the platinum fragment transfers electron density to the ruthenium centre. Similar observations were reported on the mixed-metal ferrocenylacetylides *trans*-[$(Ph_3P)_2(Ph)$-$Pt(C{\equiv}CFc)$] where the redox potential of the ferrocenyl unit is significantly lowered after introduction of the platinum fragment ($E_{\frac{1}{2}}$ of $FcC{\equiv}C$-*p*-$C_6H_4{-}CH_3$ is 0.12 V and that of *trans*-[$(Ph_3P)_2(Ph)Pt(C{\equiv}CFc)$] is −0.13 V) [34]. Complex **7** was quasi-reversibly oxidised ($\Delta E = 84$ mV) at −0.19 V indicating that the methyl cyclopentadienyl unit did not significantly ease the oxidation of the Ru centre compared to an unsubstituted cyclopentadienyl ring.

In conclusion, we have synthesised some novel mixed-metal ruthenium–osmium and ruthenium–platinum complexes. Cyclic voltammetry of these complexes shows that metal fragments can act as electron donors or acceptors and the lowest energy absorption band in the UV–vis spectra of the complexes can be optimised by changing the metal centres. The synthesis and optical spectroscopy of an extended range of mixed-metal poly-ynes are in progress in our laboratories.

4. Experimental

4.1. General

All reactions were performed under an inert nitrogen atmosphere using standard Schlenk techniques. Solvents were freshly distilled, dried and degassed before use by the standard procedures [35]. IR spectra were recorded as dichloromethane solutions, in an NaCl cell, on a Perkin-Elmer 1710 Fourier Transform spectrometer. UV–vis spectra were recorded in a Perkin-Elmer Lambda 11 spectrometer. ^{1}H-NMR and ^{31}P-{^{1}H}-NMR spectra were recorded on a Bruker WM-250 spectrometer in appropriate solvents. The chemical shifts were referenced to TMS for ^{1}H-NMR and to trimethylphosphite for ^{31}P-{^{1}H}-NMR spectra. Mass spectra were recorded as dichloromethane solutions on a Kratos MS890 spectrometer. Elemental analyses were performed at the Department of Chemistry, University of Cambridge and at the Department of Chemistry, Imperial College of Science, Technology and Medicine, London. Electrochemical data were recorded using an Autolab PGSTAT 20 potentiostat with a standard three electrode system (platinum as working and auxiliary electrodes and Ag/AgCl reference electrode). All electrochemical measurements were referenced to the ferrocene/ferrocenium redox couple (Fc = 0.50 V vs. Ag/AgCl at 298 K in 0.1 M [Bu$_4$N][BF$_4$] solution in CH$_2$Cl$_2$).

The commercially available starting materials, PEt$_3$, Ph$_2$PCH$_2$PPh$_2$ (dppm), Br-*p*-C$_6$H$_4$–Br, Br-*p*-C$_6$H$_4$–C$_6$H$_4$-*p*-Br, PhLi, CuI, Ph$_3$P, Pd(OOCCH$_3$)$_2$ were obtained from Aldrich and PtCl$_2$, RuCl$_3$·3H$_2$O from Johnson Matthey and used without further purification. Samples of HC≡CSi(CH$_3$)$_3$ were obtained from the preparation laboratory of the Department of Chemistry, University of Cambridge. The metal halides, *trans*-[(Et$_3$P)$_2$Pt(Ph)(Cl)] [36], *cis*-[(dppm)$_2$RuCl$_2$] [37], [(η^5-C$_5$H$_5$)(Ph$_3$P)$_2$RuCl] [38], [(η^5-C$_5$H$_4$–CH$_3$)(Ph$_3$P)$_2$-RuCl] [38], *cis*-[(dppm)$_2$OsCl$_2$] [37] and terminal diacetylenes HC≡C-*p*-C$_6$H$_4$–C≡CH and HC≡C-*p*-C$_6$H$_4$–C$_6$H$_4$-*p*-C≡CH were prepared by published procedures [39].

4.2. Syntheses

4.2.1. *Trans-[(dppm)$_2$Os(Cl)(C≡C-p-C$_6$H$_4$–C≡C–H)]* (**1**)

To a solution of *cis*-[Os(dppm)$_2$Cl$_2$] (0.136 g, 0.13 mmol) in dichloromethane (40 ml), H–C≡C-*p*-C$_6$H$_4$–C≡C–H (0.018 g, 0.14 mmol) and sodium hexafluorophosphate (0.043 g, 0.26 mmol) were added. The mixture was stirred for 20 h at r.t. The solution was filtered and treated with one equivalent of DBU for 3 h and the solvent was then removed in vacuo. The product was purified by washing with a few ml of dry methanol and recrystallised from dichloromethane/hexane to give a pale yellow microcrystalline powder in a 71% yield (0.106 g). Anal. calc. for C$_{60}$H$_{49}$ClP$_4$Os: C 64.36, H 4.38; Found C 63.93 H 4.76%. IR (CH$_2$Cl$_2$) ν(C≡C), 2071 cm^{-1}, ν(C≡CH) 3307 cm^{-1}. ^{1}H-NMR (CDCl$_3$, 250 Hz, δ ppm) 3.04 (s, 1H, C≡C**H**), 5.45 (m, 4H, PC**H**$_2$P), 5.91 (d, $^{3}J_{(H^2-H^3)}$ = 8 Hz, 2H, aromatic spacer protons), other aromatic spacer protons overlap with diphos. aromatics, 6.83–7.66 (m, 42H, Ph). ^{31}P-{^{1}H}-NMR (CDCl$_3$, 250 Hz, δ ppm) −190.0. FAB MS: 1120 (calc. M$^+$ 1118).

4.2.2. *Trans-[(dppm)$_2$Os(Cl)(C≡C-p-C$_6$H$_4$–C$_6$H$_4$-p-C≡C–H)]* (**2**)

The complex was obtained as for **1** as a pale yellow powder in an 87% yield. Anal. calc. for C$_{66}$H$_{53}$ClP$_4$Os·1/2CH$_2$Cl$_2$: C 64.50, H 4.36; Found C 64.45 H 4.56%. IR (CH$_2$Cl$_2$) ν(C≡C) 2071 cm^{-1}, ν(C≡CH) 3297 cm^{-1}. ^{1}H-NMR (CDCl$_3$, 250 Hz, δ ppm) 3.10 (s, 1H, C≡C**H**), 5.43 (m, 4H, PC**H**$_2$P), 6.11 (δ, $^{3}J_{(H^2-H^3)}$ = 8 Hz, 4H, aromatic spacer protons), other aromatic spacer protons overlap with diphos. aromatics, 6.80–7.54 (m, 44H, Ph). ^{31}P-{^{1}H}-NMR (CDCl$_3$, 250 Hz, δ ppm) −190.09. FAB MS: 1196 (Calc. M$^+$ 1196).

4.2.3. *Trans-[(PEt$_3$)$_2$Pt(Ph)(C≡C-p-C$_6$H$_4$–C≡C–H)]* (**3**)

A solution of *trans*-[(PEt$_3$)$_2$Pt(Ph)(Cl)] (0.350 g, 0.64 mmol) in a 1:1 mixture of dichloromethane and diethylamine (20 ml) was treated with H–C≡C-*p*-C$_6$H$_4$–C≡C–H (0.161 g, 1.28 mmol) and CuI (3 mg). The reaction mixture was stirred for 4 h at r.t. The solvent was then removed and the crude product was subjected to column chromatography on silica first using hexane (to remove any excess ligand), followed by dichloromethane-hexane (1:1) as eluants. After evaporation of solvents in vacuo the complex was obtained as an off-white solid in an 83% yield (0.340 g). Anal. calc. for C$_{28}$H$_{40}$P$_2$Pt: C 53.08, H 6.31; Found C 52.74 H 5.92%. IR (CH$_2$Cl$_2$) ν(C≡C) 2091 cm^{-1}, ν(C≡CH) 3296 cm^{-1}. ^{1}H-NMR (CDCl$_3$, 250 Hz, δ ppm) 1.08 (m, 18H, C**H**$_3$), 1.80 (m, 12H, C**H**$_2$), 3.08 (s, C≡C**H**), aromatic spacer protons overlap with phenyl aromatics, 6.7–7.4 (m, 9H, Ph). ^{31}P-{^{1}H}-NMR (CDCl$_3$, 250 Hz, δ ppm) −131.20, $^{1}J_{(\mathrm{Pt-P})}$ 2679 Hz. FAB MS: 633 (Calc. M$^+$ 633).

4.2.4. *Trans-[(dppm)$_2$(Cl)Os–C≡C-p-C$_6$H$_4$–C≡C–Ru(Cl)(dppm)$_2$]* (**4**)

To a solution of *cis*-[RuCl$_2$(dppm)$_2$] (0.071 g, 0.07 mmol) in dichloromethane (40 ml), freshly prepared *trans*-[(dppm)$_2$Os(Cl)(–C≡C–*p*-C$_6$H$_4$–C≡C–H)] (0.085 g, 0.07 mmol) and sodium hexafluorophosphate (0.023 g, 0.14 mmol) were added. The mixture was stirred for 4 h at r.t. The solution was filtered under N$_2$ and treated with one equivalent of DBU for 3 h. The solvent was then removed in vacuo. The product was purified by washing with a few ml of dry methanol to afford a reddish–yellow powder in a 45% yield (0.07 g). The complex was found to be air sensitive and this precluded accurate microanalysis. IR (CH_2Cl_2) ν(C≡C), 2075 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 250 Hz, δ ppm) 4.90 (m, 4H, Ru(PC$\mathbf{H}_2$P)), 5.44 (m, 4H, Os(PC$\mathbf{H}_2$P)), 5.95 (d, $^3J_{(H^2-H^3)} = 8$ Hz, 4H, aromatic spacer protons), 7.65 (d, $^3J_{(H^2-H^3)} = 8$ Hz, 4H, aromatic spacer protons), 6.79–7.75 (m, 80H, Ph). ^{31}P-{^{1}H} NMR ($CDCl_3$, 250 Hz, δ ppm) −147.7 (Ru($Ph_2\mathbf{P}CH_2\mathbf{P}Ph_2$)), −190.20 (Os($Ph_2PCH_2PPh_2$)). FAB MS: 2022 (Calc. M^+ 2021).

4.2.5. Trans-[(dppm)$_2$(Cl)Ru–C≡C-p-C$_6$H$_4$–C≡C–Pt(Et$_3$P)$_2$(Ph)] (**5**)

The complex was obtained, as for **4** (except that *trans*-[(PEt_3)$_2$Pt(Ph)(C≡C-*p*-C_6H_4–C≡C–H) was used), as a pale yellow powder in an 85% yield. The crude powder was redissolved in of 1:4 dichloromethane/hexane (40 ml) and the solvent was evaporated slowly at r.t. on a rotary evaporator until a reddish oil appeared in the flask. The supernant liquid was decanted and this process was repeated once or twice, to leave, after evaporation of solvents in vacuo, a bright yellow solid. Anal. calc. for $C_{78}H_{83}ClP_6RuPt$: C 60.91, H 5.40; Found C 60.64 H 5.34%. IR (CH_2Cl_2) ν(C≡C), 2075, 2091 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 250 Hz, δ ppm) 1.08 (m, 18H, C$\mathbf{H}_3$), 1.72 (m, 12H, C$\mathbf{H}_2$), 4.91 (m, 4H, PC$\mathbf{H}_2$P), aromatic spacer protons overlap with diphos. aromatics, 6.7–7.4 (m, 49H, Ph). ^{31}P-{^{1}H}-NMR ($CDCl_3$, 250 Hz, δ ppm) −131.38 ($^1J_{(Pt-P)}$ 2688 Hz, Pt($\mathbf{P}Et_3$)), −147.48 (Ru($Ph_2\mathbf{P}CH_2\mathbf{P}Ph_2$)). FAB MS: 1537 (Calc. M^+ 1536).

4.2.6. Trans-[(η^5-C$_5$H$_5$)(PPh$_3$)$_2$Ru–C≡C-p-C$_6$H$_4$–C≡C–Pt(Et$_3$P)$_2$(Ph)] (**6**)

A refluxing solution of [(η^5-C_5H_5)($\mathbf{P}Ph_3$)$_2$RuCl] (0.100 g, 0.137 mmol) in dry methanol (15 ml) was treated with *trans*-[(PEt_3)$_2$Pt(Ph)(C≡C-*p*-C_6H_4–C≡C–H)] (0.094 g, 0.15 mmol) and refluxed for 10 min. It was then allowed to cool down to r.t. and sodium (10-fold excess) was added. On stirring a yellow precipitate appeared which was filtered through a sintered funnel to afford a analytically pure yellow powder in a 49% yield (0.115 g). Anal. calc. for $C_{69}H_{74}P_4RuPt$: C 62.62, H 5.64; Found C 62.35 H 5.27%. IR (CH_2Cl_2) ν(C≡C), 2070, 2092 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 250 Hz, δ ppm) 0.95 (m, 18H, C$\mathbf{H}_3$), 1.73 (m, 12H, C$\mathbf{H}_2$), 4.47 (s, 5H, $C_5\mathbf{H}_5$), aromatic spacer protons overlap with phos. aromatics, 6.85–7.80 (m, 39H, Ph). ^{31}P-{^{1}H}-NMR ($CDCl_3$, 250 Hz, δ ppm) −131.41, ($^1J_{(Pt-P)}$ 2695 Hz, Pt($\mathbf{P}Et_3$)), −89.94 (Ru($\mathbf{P}Ph_3$)). FAB MS: 1325 (Calc. M^+ 1324).

4.2.7. Trans-[(Et$_3$P)$_2$(Ph)Pt–C≡C–C$_6$H$_4$-p-C≡C–Ru(Ph$_3$P)$_2$(η^5-C$_5$H$_4$–CH$_3$)] (**7**)

This was obtained as an analogous fashion to **6** as a yellow power, yield: 66%. Anal. calc. for $C_{70}H_{76}P_4RuPt$: C 62.87, H 5.68; Found C 62.36 H 5.41%. IR (CH_2Cl_2) ν(C≡C), 2069, 2090 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 250 Hz, δ ppm) 1.07 (m, 18H, C$\mathbf{H}_3$), 1.76 (m, 12H, C$\mathbf{H}_2$), 2.02 (s, 3H, C$\mathbf{H}_3$), 3.93 (s, 2H, $C_5\mathbf{H}_4$), 3.79(s, 2H, $C_5\mathbf{H}_4$), aromatic spacer protons overlap with phos. aromatics, 7.03–7.50 (m, 39H, Ph). ^{31}P-{^{1}H}-NMR ($CDCl_3$, 250 Hz, δ ppm) −131.29, ($^1\mathbf{J}_{(Pt-P)}$ 2647 Hz, Pt($\mathbf{P}Et_3$)), −89.67 (Ru($\mathbf{P}Ph_3$)). FAB MS: 1337 (Calc. M^+ 1336.5).

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