

Synthesis and characterisation of mono-acetylide and unsymmetrical bis-acetylide complexes of ruthenium and osmium: X-ray structure determinations on $[(dppe)_2Ru(Cl)(C\equiv C-C_6H_4-p-NO_2)]$, $[(dppe)_2Ru(Cl)(C\equiv C-C_6H_3-o-CH_3-p-NO_2)]$ and $[(dppm)_2Os(C\equiv C-C_6H_4-p-CH_3)(C\equiv C-C_6H_4-p-NO_2)]$

Muhammad Younus ^a, Nicholas J. Long ^{a,*}, Paul R. Raithby ^b, Jack Lewis ^b, Nicola A. Page ^b, Andrew J.P. White ^a, David J. Williams ^a, Michael C.B. Colbert ^b, Andrew J. Hodge ^b, Muhammad S. Khan ^c, David G. Parker ^d

^a Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, SW7 2AY, London, UK

^b Department of Chemistry, Lensfield Road, CB2 1EW, Cambridge, UK

^c Department of Chemistry, College of Science, Sultan-Qaboos University, 123 Al-Khod, Oman

^d ICI Group R & T Affairs, P.O. 90, Wilton Centre, TS90 8JE, Middlesborough, Cleveland, UK

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Abstract

The synthesis of a series of metal mono-acetylides *trans*- $[(dppe)_2Ru(Cl)(C\equiv C-R)]$ ($R = C_6H_4-p-C_6H_5$, $C_6H_4-p-CH_3$, $C_6H_4-p-NO_2$, $C_6H_3-o-CH_3-p-NO_2$, $dppe = Ph_2PCH_2CH_2PPh_2$), and unsymmetrical metal bis-acetylides *trans*- $[(dppm)_2M(C\equiv C-R)(C\equiv C-R')]$; ($M = Ru, Os$; $R = C_6H_4-p-NO_2$, $R' = C_6H_5$, $C_6H_4-p-CH_3$; $R = C_6H_5$, $R' = C_6H_4-p-CH_3$) using a variety of σ -acetylide coupling reactions is reported. Three compounds have been structurally characterised, including the unsymmetrical *trans*- $[(dppm)_2Os(C\equiv C-R)(C\equiv C-R')]$ ($R = C_6H_4-p-CH_3$, $R' = C_6H_4-p-NO_2$) which shows the 'rigid-rod' nature of the acetylide-metal-acetylide linkage. The electrochemistry of symmetrical and unsymmetrical Ru(II) complexes demonstrates the role of the acetylide and the auxiliary ligands in determining the ease of oxidation at the metal centre whilst UV-vis spectral changes illustrate the influence of electron-withdrawing and -donating ligands. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The development of synthetic routes towards organometallic metal-acetylide oligomers and polymers has progressed rapidly following the initial reports on Group 10 metal-acetylide polymers [1]. Since then, there has been a burgeoning range of ligands and metals incorporated into these ligand systems [2]. The driving force behind these synthetic developments has

been the requirement of new products for the materials industry and these linear, delocalised species are potentially liquid crystalline [3], conductive (with electron transfer) [4], and third-order non-linear optical materials [5]. Compounds need to be processable and characterisable and it is clear that greater variation needs to be introduced into the p-conjugated bi- or multi-metallic systems [6], e.g. incorporation of metals of different oxidation state and variation of phosphines (the bulkier the phosphine, the greater the solubility of the polymer). Our group has recently formed species featuring d^6 , d^7 and d^8 metals in order to increase the flexibility of the systems [7].

* Corresponding author. Tel.: +44-171-5945-781; fax: +44-171-5945-804.

E-mail address: n.long@ic.ac.uk (N.J. Long)

Design of molecules with symmetric and unsymmetric donor/acceptor end groups at *para* positions continues to draw much attention due to their intriguing third- and second-order nonlinear optical behaviour [8].

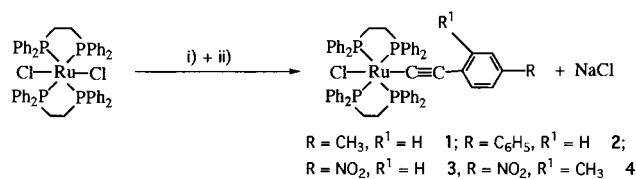
Group 8 metal acetylides of the type *trans*-[(L-L)₂M(Cl)(C≡C-R)] (L-L = dppe and/or dppe; M = Ru and/or Os) has recently been reported by several groups [9,10] including ourselves [6j, 7d–h]. Following our previous work, we have synthesised and studied the coupling reactions of these complexes with various acetylenic ligands which give rise to unsymmetrical bis-acetylide complexes. We, therefore report here, the synthesis of a series of mono-acetylide complexes of the {Ru(II)(dppe)} fragment along with some bis-acetylide complexes of {ML₂} (M = Ru, Os; L = dppe, dppe) in which the metal fragment contains symmetric and unsymmetric σ -acetylide linkages in a *trans* configuration. Single crystal X-ray determinations have been made of the mono-acetylide complexes *trans*-[(dppe)₂Ru(Cl)(C≡C-C₆H₄-*p*-NO₂)] and *trans*-[(dppe)₂Ru(Cl)(C≡C-C₆H₃-*o*-CH₃-*p*-NO₂)] and the unsymmetrical bis-acetylide complex *trans*-[(dppm)₂Os(C≡C-C₆H₄-*p*-NO₂)(C≡C-C₆H₄-*p*-CH₃)]. All the complexes have been fully characterised and in particular, studied for their electrochemical and electronic properties.

2. Results and discussion

2.1. Synthetic studies

2.1.1. Mono-acetylides of ruthenium

Although aryl substituted mono-acetylide complexes *trans*-[(dppm)₂Ru(Cl)(C≡C-R)] (R = C₆H₄-*p*-CH₃, C₆H₄-*p*-C₆H₅, C₆H₄-*p*-NO₂, C₆H₃-*o*-CH₃-*p*-NO₂), can be formed in good yield by the reaction of *cis*-[(dppm)₂RuCl₂] with terminal acetylenes [7e] using Dixneuf's route [9b], we found that this was not a good route for formation of the Ru(dppe)₂ analogues. This is because, despite our efforts, *cis*-[(dppe)₂RuCl₂] could not be synthesised in a pure form (it being contaminated with *trans*-[(dppe)₂RuCl₂]). The *cis*- to *trans*-isomerisation during the acetylide addition is believed to be a driving force of the reaction however, the *trans*-starting material [(dppe)₂RuCl₂] reacts with terminal acetylenes albeit slowly [6j]. Therefore, *trans*-[(dppe)₂RuCl₂] was treated with the terminal acetylenes HC≡CR (R = C₆H₄-*p*-CH₃, C₆H₄-*p*-C₆H₅, C₆H₄-*p*-NO₂, C₆H₃-*o*-CH₃-*p*-NO₂) in CH₂Cl₂ in the presence of two equivalents of NaPF₆ for 5–7 days at room temperature (r.t.), to form the vinylidene complexes [(dppe)₂(Cl)Ru=C=C(H)(R)]⁺[PF₆]⁻ which were not characterised but reacted in situ. After removal of excess ligands by washing with hexane, one equivalent of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in CH₂Cl₂ was added and stirring continued for 3 h to afford the

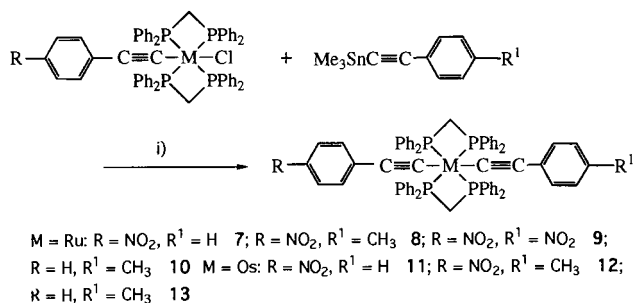


Scheme 1. Synthesis of ruthenium(II) mono-acetylides.

acetylide complexes *trans*-[(dppe)₂Ru(Cl)(C≡C-R)] (R = C₆H₄-*p*-CH₃ **1**, C₆H₄-*p*-C₆H₅ **2**, C₆H₄-*p*-NO₂ **3**, C₆H₃-*o*-CH₃-*p*-NO₂ **4**) (Scheme 1). In recent reports, Dixneuf et al. independently describe the synthesis of *trans*-[(dppe)₂Ru(Cl)(-C≡C-R)] (R = H, ^tBu, Ph, C₆H₄-*p*-OMe, C₆H₄-*p*-NO₂) using *cis*-[(dppe)₂RuCl₂] as the starting material [9d]. Although the reaction of *trans*-[(dppe)₂RuCl₂] with terminal acetylenes is slower than with the *cis*-analogues, the former material has easier availability and gives high yielding selective syntheses of mono-acetylides.

2.1.2. Unsymmetrical bis-acetylides of Ru(II) and Os(II)

Following our previous method, [6j] we have synthesised a series of unsymmetrical bis-acetylides *trans*-[(dppm)₂Ru(C≡CR)(-C≡CR')] (M = Ru and Os) by the reaction of metal chloro-mono-acetylides with trimethylstannyl acetylides. For example, when *trans*-[(dppm)₂Ru(Cl)(-C≡C-*p*-C₆H₄-NO₂)] was treated with Me₃SnC≡CR (R = C₆H₅, C₆H₄-*p*-CH₃) in THF, in the presence of CuI, under reflux for 2 h, a mixture of unsymmetrical bis-acetylides *trans*-[(dppm)₂Ru(C≡C-*p*-C₆H₄-NO₂)(C≡CR)] (R = C₆H₅ **7**, C₆H₄-*p*-CH₃ **8**) and symmetrical bis-acetylide *trans*-[(dppm)₂Ru(-C≡C-*p*-C₆H₄-NO₂)₂] **9** was formed (Scheme 2) (complexes **7** and **9** have recently been formed by a different method in 30, and 62% yields, respectively [10b], whilst our work was in progress). The products can be separated by column chromatography on neutral grade II alumina using hexane/dichloromethane mixtures as eluents and the yields of the unsymmetrical acetylides were much higher (ca. 50%) than the symmetrical one (<20%). The symmetrical bis-acetylide may be formed by a disproportionation mechanism, and this has been ob-



Scheme 2. Synthesis of unsymmetrical ruthenium(II) and osmium(II) bis-acetylides.

Table 1
Infrared, $^{31}\text{P}\{^1\text{H}\}$ -NMR and mass spectra of ruthenium(II) and osmium(II) mono- and bis-acetylides

Complex	$\nu(\text{C}\equiv\text{C})^a$ (cm^{-1})	$^{31}\text{P}\{^1\text{H}\}$ -NMR ^b (ppm)	M^{+c}
<i>trans</i> -[(dppe) ₂ Ru(Cl)(C≡C-C ₆ H ₄ - <i>p</i> -CH ₃)] 1	2074	-91.3	1048.2 (1048.5)
<i>trans</i> -[(dppe) ₂ Ru(Cl)(C≡C-C ₆ H ₄ - <i>p</i> -C ₆ H ₅)] 2	2071	-91.3	1110 (1110)
<i>trans</i> -[(dppe) ₂ Ru(Cl)(C≡C-C ₆ H ₄ - <i>p</i> -NO ₂)] 3	2051	-92.5	1079 (1079)
<i>trans</i> -[(dppe) ₂ Ru(Cl)(C≡C-C ₆ H ₃ - <i>o</i> -CH ₃ - <i>p</i> -NO ₂)] 4	2029	-91.4	1094 (1093.5)
<i>trans</i> -[(dppe) ₂ Ru(C≡C-C ₆ H ₄ - <i>p</i> -CH ₃) ₂] 5	2062	-87.1	-
<i>trans</i> -[(dppe) ₂ Ru(C≡C-C ₆ H ₄ - <i>p</i> -NO ₂) ₂] 6	2043	-88.2	-
<i>trans</i> -[(dppm) ₂ Ru(C≡C-C ₆ H ₄ - <i>p</i> -NO ₂)(C≡C-C ₆ H ₅)] 7	2054, 2079	-144.9	1116 (1116)
<i>trans</i> -[(dppm) ₂ Ru(C≡C-C ₆ H ₄ - <i>p</i> -NO ₂)(C≡C-C ₆ H ₄ - <i>p</i> -CH ₃)] 8	2054, 2080	-145.0	1131 (1130)
<i>trans</i> -[(dppm) ₂ Ru(C≡C-C ₆ H ₄ - <i>p</i> -NO ₂) ₂] 9	2052	-145.2	1162 (1161)
<i>trans</i> -[(dppm) ₂ Ru(C≡C-C ₆ H ₅)(C≡C-C ₆ H ₄ - <i>p</i> -CH ₃)] 10	2069	-144.5	1083 (1085)
<i>trans</i> -[(dppm) ₂ Os(C≡C-C ₆ H ₄ - <i>p</i> -NO ₂)(C≡C-C ₆ H ₅)] 11	2052, 2080	-191.4	1209 (1207)
<i>trans</i> -[(dppm) ₂ Os(C≡C-C ₆ H ₄ - <i>p</i> -NO ₂)(C≡C-C ₆ H ₄ - <i>p</i> -CH ₃)] 12	2051, 2083	-191.4	1218 (1221)
<i>trans</i> -[(dppm) ₂ Os(C≡C-C ₆ H ₅)(C≡C-C ₆ H ₄ - <i>p</i> -CH ₃)] 13	2069	-195.0	1178 (1175)

^a IR spectra were recorded in CH₂Cl₂.

^b $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra were referenced to P(OMe)₃.

^c Calculated molecular ions are given in parentheses.

served in analogous systems [9d, 10b] but surprisingly in each case and also here, only one symmetrical bis-acetylide species was observed as opposed to the two that are possible. In a similar reaction, *trans*-[(dppm)₂Ru(Cl)(C≡C-C₆H₅)] was reacted with Me₃SnC≡C-*p*-C₆H₄-CH₃ in THF to form *trans*-[(dppm)₂Ru(C≡C-*p*-C₆H₄-CH₃)(-C≡C-C₆H₅)] **10** in 44% yield but no trace of symmetrical product was observed in the reaction mixture. Unsymmetrical osmium bis-acetylides *trans*-[(dppm)₂Os(C≡C-*p*-C₆H₄-NO₂)(C≡CR)] (R = C₆H₅ **11**, C₆H₄-*p*-CH₃ **12**) and *trans*-[(dppm)₂Os(C≡C-*p*-C₆H₄-CH₃)(C≡C-C₆H₅)] **13** were similarly prepared by the reaction of osmium chloro-mono-acetylides with the appropriate tin acetylides although the reactions were slower than those of ruthenium analogues. The products were purified by column chromatography on neutral grade II alumina using hexane/dichloromethane mixtures as eluents followed by recrystallisation in a solvent mixture of dichloromethane and hexane (1:1).

Unsymmetrical bis-acetylide complexes of the type *trans*-[(dppe)₂Ru(C≡CR)(C≡CR')] (R = Ph, R' = *n*Bu; R = Ph, R' = *p*-C₆H₄-NO₂; R = *n*Bu, R' = *p*-C₆H₄-NO₂; R = *p*-C₆H₄-OMe, R' = *p*-C₆H₄-NO₂) can also be formed by the reaction of [(dppe)₂(Cl)Ru=C=C(H)(R')] + [PF₆]⁻ with HC≡CR', NaPF₆ and NEt₃ (reported by Touchard et al. independently [9d] during the preparation of this manuscript). Following this procedure, [(dppm)₂(Cl)Ru=C=C(H)(Ph)] + [PF₆]⁻ was reacted with HC≡C-*p*-C₆H₄-NO₂. Unsymmetrical bis-acetylide **7** (33%) and symmetrical bis-acetylide **9** (15%) were obtained and purified by column chromatography on alumina.

Unsymmetrical bis-acetylides of platinum, *trans*-[(Et₃P)₂Pt(C≡C-R)(C≡CR')] (R = Me, Ph; R' = H) were first made by Sebal et al. [11] by the reaction of *trans*-[(Et₃P)₂Pt(Cl)(-C≡C-R)] with Me₃SnC≡CR'. A

slow conversion of unsymmetrical to symmetrical acetylides in solution was observed and was believed to be accelerated in the presence of Me₃SnCl. However, in the case of ruthenium and osmium, no such conversion was observed, even when unsymmetrical bis-acetylides were refluxed in dichloromethane for 48 h in the presence of Me₃SnCl.

Symmetrical and unsymmetrical bis-acetylides of ruthenium [(depe)₂Ru(C≡C-C₆H₅)₂], [(depe)₂Ru(C≡C-C₆H₄-*p*-OMe)₂] and [(depe)₂Ru(C≡C-C₆H₅)(C≡C-C₆H₄-*p*-OMe)] (depe = Et₂PCH₂CH₂PEt₂) complexes have also been reported by Field and co-workers [6p]. These were formed as a mixture by the reaction *trans*-[(depe)₂RuCl₂] with two different acetylenes, in the presence of sodium methoxide. The amount of the unsymmetrical bis-acetylides formed was dependent on the ratio of the terminal acetylenes used in the reactions.

2.2. Spectroscopic characterisation

The $\nu(\text{C}\equiv\text{C})$ stretching frequency is diagnostic in the characterisation of metal acetylide complexes. All the ruthenium and osmium acetylides showed a single stretching frequency in the range of 2029–2081 cm⁻¹ for $\nu(\text{C}\equiv\text{C})$ bonds which confirms the *trans* configuration of acetylides around metal atoms with respect to other acetylides or chlorides (Table 1). In the case of metal mono-acetylides, the $\nu(\text{C}\equiv\text{C})$ stretching frequency of the NO₂-substituted aryl acetylides is lower in wavenumber than those of phenyl or tolyl species. This is due to the higher degree of electron delocalisation when electron-withdrawing NO₂ occupies the *para* position of the aryl ring. Interestingly, when an electron donating methyl group is added to the nitrophenyl acetylides the frequency decreases. The $\nu(\text{C}\equiv\text{C})$ stretch-

ing frequencies of the symmetrical bis-acetylides of ruthenium are ca. 10 cm^{-1} lower than those of mono-acetylides and in most cases, the unsymmetrical bis-acetylides showed two different $\nu(\text{C}\equiv\text{C})$ stretching frequencies indicative of the different types of acetylides.

All the ruthenium and osmium acetylides showed broad multiplets in the range ca. 6.7–7.8 ppm in their $^1\text{H-NMR}$ spectra which are due to the phenyl protons of the chelating phosphine ligands. For complexes **1–6**, multiplets appeared at ca. 2.6 ppm which we assign to the CH_2 protons of the ruthenium bound dppe ligand. In the case of dpmm bound ruthenium complexes **7–10**, the CH_2 protons resonate at ca. 4.8 ppm. In most cases, acetylide aromatic protons show the expected $(\text{AB})_2$ pattern. For example, complex **3** shows two sets of doublets at 6.43 and 7.93 ppm with a coupling constant of $^3J(\text{AB}) = 9\text{ Hz}$. All the complexes displayed a singlet in their $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum which again suggested that the acetylide ligands adopt a *trans* configuration with respect to the chloride or other acetylide. The phosphorus atoms in *trans*-[(dppe) $_2$ RuCl $_2$] resonate at -96 ppm . This signal shifts downfield by ca. 4 ppm when one Cl^- is substituted by an acetylide, and it resonates further downfield by ca. 6 ppm when the second Cl^- is substituted (Table 1). A similar trend was observed in the spectra of the metal acetylide complexes with dpmm ligands and suggests that acetylide ligands have greater π -electron accepting ability than that of the chloride ligands.

Most of the metal (Ru and Os) acetylide complexes showed a molecular ion peak in their $+ \text{FAB}$ mass spectra (Table 1). In some cases molecular ions were not present but fragmented $[\text{M}-\text{C}\equiv\text{C}-\text{R}]^+$ ions were observed indicating the presence of the complexes. In the mass spectra of the complexes *trans*-[(dppe) $_2$ Ru(Cl)(C \equiv C-R)] **1–4**, stepwise loss of chlorides and acetylides was observed and in the spectra of the corresponding bis-acetylides **5–6**, stepwise loss of two acetylide fragments was seen. For the unsymmetrical bis-acetylides, the fragmentation pattern was often associated with the stepwise loss of different acetylide ligands.

Metal to acetylide charge transfer is a common spectral feature of metal acetylide complexes and reflects the π -electron conjugation in these complexes. [12] The UV–vis spectra of the ruthenium and osmium acetylide complexes have been studied to investigate the effect of (i) electron donor and acceptor acetylides, (ii) different auxiliary phosphine ligands on metal centres and (iii) different metals. The lowest energy band of the complexes is listed in Table 2. The metal acetylides, *trans*-[(dpmm) $_2$ M(Cl)(C \equiv C-C $_6$ H $_5$)] (M = Ru) and (M = Os) displayed the lowest energy bands at around 315 nm which were assigned as metal to acetylide charge transfer. Replacement of aryl 4-H by 4-NO $_2$ gave rise to a

large shift to lower wavenumber (160 nm for Ru and 189 nm for Os) which may be due to some contribution from vinylidene-type structures (M=C=C=C-). Calculations on similar ruthenium bis-acetylide systems showed that changing the C \equiv C (acetylide) to C=C (vinylidene) provides a better energy match between the π -orbital of the ethylene and π -orbital of the phenyl ring. This lowers the energy of the LUMO and the energy of the HOMO is not greatly affected and thus decreases the band gap [12a]. Substitution of the remaining chloride of *trans*-[(dpmm) $_2$ Ru(Cl)(C \equiv C-R)] by a donor tolyl acetylide did not have much (shifted to lower frequency by only 7 nm) effect on the lowest energy band of the complexes (Fig. 1). Replacement of the auxiliary phosphine Ph $_2$ PCH $_2$ PPh $_2$ by Ph $_2$ PCH $_2$ CH $_2$ PPh $_2$ did not have a significant effect on the lowest energy band either but this band was shifted significantly to a lower wave number when ruthenium was replaced by osmium. The occurrence of significant solvatochromism is often an indicator of a high molecular hyperpolarisability, β , and has for example been demonstrated for some conjugated organoferrocenes [13]. The solvatochromism of the donor- and acceptor-based unsymmetrical ruthenium and osmium bis-acetylides was studied by varying solvents of different polarity and the results are listed in Table 3. In each complex, a moderate shift to lower frequency of the lowest energy band was observed and osmium acetylides showed greater shift than ruthenium species.

Table 2

UV–vis spectral data of ruthenium and osmium mono- and bis-acetylides

Compound	λ_{max}^a (nm)	log ϵ
HC \equiv C-Ph	246	4.22
HC \equiv C-C $_6$ H $_4$ - <i>p</i> -CH $_3$	251	4.18
HC \equiv C-C $_6$ H $_4$ - <i>p</i> -NO $_2$	286	4.13
<i>trans</i> -[(dpmm) $_2$ Ru(Cl)(C \equiv C-Ph)]	316	4.19
<i>trans</i> -[(dpmm) $_2$ Ru(Cl)(C \equiv C-C $_6$ H $_4$ - <i>p</i> -CH $_3$)]	313	4.14
<i>trans</i> -[(dpmm) $_2$ Ru(Cl)(C \equiv C-C $_6$ H $_4$ - <i>p</i> -NO $_2$)]	476	4.21
<i>trans</i> -[(dpmm) $_2$ Ru(C \equiv CPh)]	480	4.26
(C \equiv C-C $_6$ H $_4$ - <i>p</i> -NO $_2$)] 7		
<i>trans</i> -[(dpmm) $_2$ Ru(C \equiv C-C $_6$ H $_4$ - <i>p</i> -CH $_3$)]	483	4.25
(C \equiv C-C $_6$ H $_4$ - <i>p</i> -NO $_2$)] 8		
<i>trans</i> -[(dpmm) $_2$ Ru(C \equiv CPh)]	320	4.47
(C \equiv C-C $_6$ H $_4$ - <i>p</i> -CH $_3$)] 10		
<i>trans</i> -[(dppe) $_2$ Ru(Cl)(C \equiv C-C $_6$ H $_4$ - <i>p</i> -NO $_2$)] 3	483	4.28
<i>trans</i> -[(dppe) $_2$ Ru(Cl)(C \equiv C-C $_6$ H $_3$ - <i>o</i> -CH $_3$ - <i>p</i> -NO $_2$)] 4	491	4.20
<i>trans</i> -[(dpmm) $_2$ Os(Cl)(C \equiv C-Ph)]	312	4.41
<i>trans</i> -[(dpmm) $_2$ Os(Cl)(C \equiv C-C $_6$ H $_4$ - <i>p</i> -NO $_2$)]	501	4.27
<i>trans</i> -[(dpmm) $_2$ Os(C \equiv CPh)]	499	4.31
(-C \equiv C-C $_6$ H $_4$ - <i>p</i> -NO $_2$)] 11		

^a Spectra were recorded in CH $_2$ Cl $_2$ solutions.

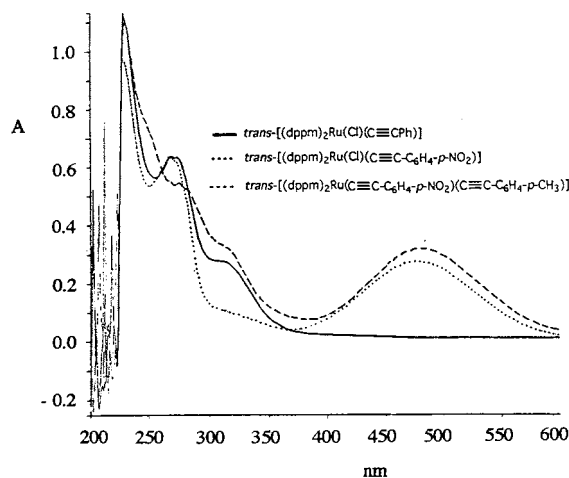


Fig. 1. The lowest energy absorption bands in the UV-vis spectra of some ruthenium(II) mono- and bis-acetylides.

2.3. X-ray crystallography

Single, X-ray quality crystals of $[(dppe)_2Ru(Cl)(C\equiv C-C_6H_4-p-NO_2)]$ **3**, $[(dppe)_2Ru(Cl)(C\equiv C-C_6H_3-o-CH_3-p-NO_2)]$ **4** and $[(dppm)_2Os(C\equiv C-C_6H_4-p-CH_3)(C\equiv C-C_6H_4-p-NO_2)]$ **12** were obtained by diffusion of hexane into a dichloromethane solution. The molecular structures of **3**, **4** and **12** are shown in Figs. 2–4, respectively, and selected bond parameters for each structure are listed in Tables 4–6, respectively. In **3**, ruthenium is octahedrally coordinated by two chelating phosphines, i.e. $Ph_2PCH_2CH_2PPh_2$, one chloride and one acetylide. The four phosphorus atoms occupy the equatorial plane of the octahedron and the chloride and acetylide adopt *trans* positions with respect to each other. This geometry is consistent with that of other recently reported ruthenium acetylides. The $C\equiv C$ bond distance is 1.206(7) Å which is longer than that of the

Table 3
Solvatochromism studies of some ruthenium and osmium bis-acetylides

Solvent	λ_{max} of 7 ^b (nm)	λ_{max} of 8 ^c (nm)	λ_{max} of 11 ^d (nm)
Ethylacetate	464	467	480
Methanol	^a	^a	495
Acetone	474	475	493
Ethanol	^a	^a	501
Chloroform	485	487	506
Dichloro- methane	480	484	499
Dimethyl- formamide	482	486	504

^a Insoluble in the examining solvents.

^b **7**, $trans-[(dppm)_2Ru(C\equiv C-Ph)(C\equiv C-C_6H_4-p-NO_2)]$.

^c **8**, $trans-[(dppm)_2Ru(C\equiv C-C_6H_4-p-CH_3)(C\equiv C-C_6H_4-p-NO_2)]$.

^d **11**, $trans-[(dppm)_2Os(C\equiv C-Ph)(C\equiv C-C_6H_4-p-NO_2)]$.

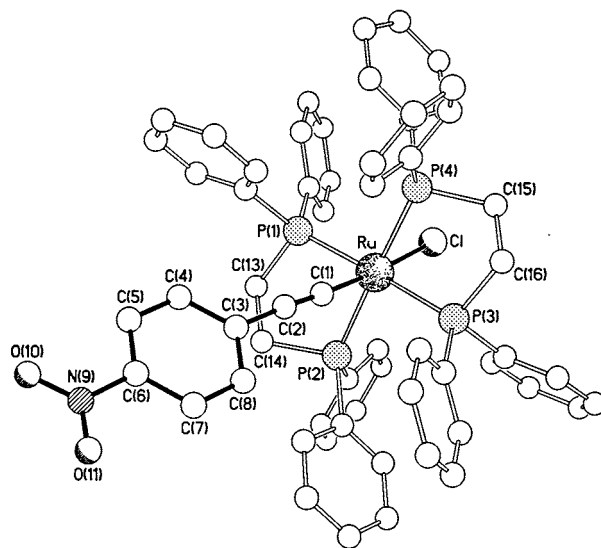


Fig. 2. Molecular structure of $[(dppe)_2Ru(Cl)(C\equiv C-C_6H_4-p-NO_2)]$ **3**.

previously reported $[(dppe)_2Ru(Cl)(C\equiv C-C_6H_5)]$ complex [6j]. The electron withdrawing NO_2 group removes electron density from the $Ru-C\equiv C$ system, thus making the $C\equiv C$ bond distance longer. This observation is consistent with the IR spectral data as the IR stretching frequency of the $C\equiv C$ group was shifted to higher frequency by 21 cm^{-1} when aryl 4-H was replaced by NO_2 . The $Cl-Ru-C$ and $M-C-C$ bond angles are $176.2(1)^\circ$, and $175.3(4)^\circ$, respectively, which indicates that the metal acetylides maintain linearity with respect to Cl^- .

The $Ru(II)$ centre also displays the expected octahedral coordination in **4** but introduction of a CH_3 group in the *ortho* position of the substituted aryl unit changes the electron density distribution in the $Ru-C$ and $C\equiv C$

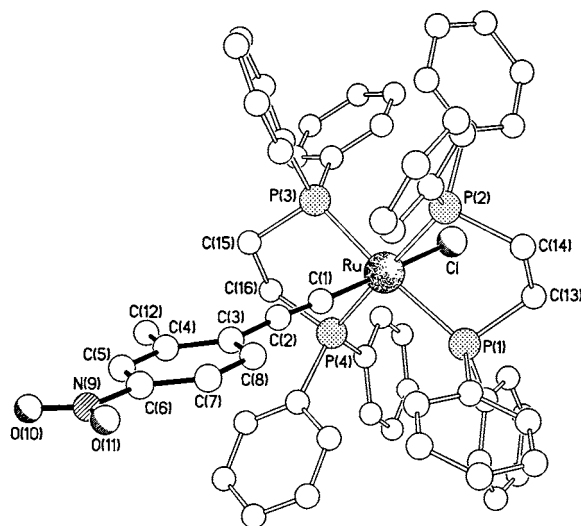


Fig. 3. Molecular structure of $[(dppe)_2Ru(Cl)(C\equiv C-C_6H_3-o-CH_3-p-NO_2)]$ **4**.

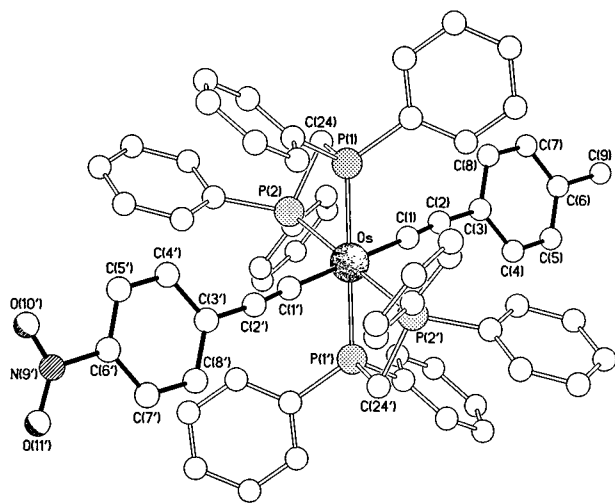


Fig. 4. Molecular structure of $[(dppm)_2Os(C\equiv C-C_6H_4-p-NO_2)(C\equiv C-C_6H_4-p-CH_3)]$ **12**.

bonds from those in $[(dppe)_2Ru(Cl)(C\equiv C-C_6H_4-p-NO_2)]$ **3**. The Ru–C bonds get longer, suggesting that ligand to metal or metal to ligand charge transfer is greater in this complex than that in $[(dppe)_2Ru(Cl)(C\equiv C-C_6H_5)]$ and **3**. The IR spectrum of the complex also supports this fact by showing a shift to higher frequency in the $\nu(C\equiv C)$ stretching vibration (Table 1). The metal to phosphorus bond lengths lie in the range 2.364(3)–2.409(3) Å, the metal to carbon bond length of the acetylide ligand is 2.013(11) Å and the C=C bond length is 1.19(1) Å. These values are similar to those found for **3**.

The X-ray analysis of **12** shows it to crystallise with a triclinic unit cell that is essentially the same as those reported previously for the dinitro [10b] and the nitro/phenyl [10c] analogues. The dinitro species was

Table 4
Selected bond lengths (Å) and angles (°) for $[(dppe)_2Ru(Cl)(C\equiv C-C_6H_4-p-NO_2)]$ **3**

Bond length (Å)			
Ru–C(1)	1.986(5)	Ru–P(1)	2.360(2)
Ru–P(2)	2.354(1)	Ru–P(3)	2.366(2)
Ru–P(4)	2.386(1)	Ru–Cl	2.500(1)
C(1)–C(2)	1.206(7)	C(2)–C(3)	1.442(7)
Bond angles (°)			
C(1)–Ru–P(2)	80.70(14)	C(1)–Ru–P(1)	87.00(13)
P(2)–Ru–P(1)	83.23(6)	C(1)–Ru–P(3)	91.98(13)
P(2)–Ru–P(3)	95.52(6)	P(1)–Ru–P(3)	178.51(4)
C(1)–Ru–P(4)	98.83(14)	P(2)–Ru–P(4)	178.04(4)
P(1)–Ru–P(4)	98.66(6)	P(3)–Ru–P(4)	82.58(6)
C(1)–Ru–Cl	176.20(13)	P(2)–Ru–Cl	100.70(5)
P(1)–Ru–Cl	89.65(5)	P(3)–Ru–Cl	91.40(5)
P(4)–Ru–Cl	79.89(5)	C(2)–C(1)–Ru	175.3(4)
C(1)–C(2)–C(3)	174.4(5)		

Table 5
Selected bond lengths (Å) and angles (°) for $[(dppe)_2Ru(Cl)(C\equiv C-C_6H_5-o-CH_3-p-NO_2)]$ **4**

Bond length (Å)			
Ru–C(1)	2.013(11)	Ru–P(3)	2.364(3)
Ru–P(4)	2.365(3)	Ru–P(2)	2.405(3)
Ru–P(1)	2.409(3)	Ru–Cl	2.473(3)
C(1)–C(2)	1.189(14)	C(2)–C(3)	1.470(2)
Bond angles (°)			
C(1)–Ru–P(3)	86.6(3)	C(1)–Ru–P(4)	83.1(3)
P(3)–Ru–P(4)	82.93(12)	C(1)–Ru–P(2)	98.5(3)
P(3)–Ru–P(2)	98.07(12)	P(4)–Ru–P(2)	178.14(12)
C(1)–Ru–P(1)	99.8(3)	P(3)–Ru–P(1)	173.58(12)
P(4)–Ru–P(1)	97.59(12)	P(2)–Ru–P(1)	81.24(11)
C(1)–Ru–Cl	175.3(3)	P(3)–Ru–Cl	90.97(11)
P(4)–Ru–Cl	92.53(12)	P(2)–Ru–Cl	85.89(11)
P(1)–Ru–Cl	82.61(11)	C(2)–C(1)–Ru	175.9(10)
C(1)–C(2)–C(3)	171.3(12)		

shown to have an ordered structure in the centrosymmetric space group $P\bar{1}$ (no. 2) whereas the nitro/phenyl compound was considered to be disordered about an inversion centre at the metal atom. In the current nitro/toluene structure a similar problem is present with only the terminal nitro and methyl substituents breaking the inversion symmetry. Attempts to desymmetrise the structure by refining in the non-centrosymmetric space group $P1$ (no. 1) led to substantial ‘ghosting’ in the residual electron density maps and instability in the refinements. These could not be rectified by the imposition of bonding constraints and/or damping and thus we were forced to conclude that the structure was genuinely disordered with reversals of the directions of the *p*-nitrophenylethynyl and the *p*-tolylethynyl ligands throughout the crystal.

The geometry at osmium is distorted octahedral with the principal distortions (70.15(4)°) being associated with the bite of the chelating phosphine. The

Table 6
Selected bond lengths (Å) and angles (°) for $[(dppm)_2Os(C\equiv C-C_6H_4-p-NO_2)(C\equiv C-C_6H_4-p-CH_3)]$ **12**

Bond length (Å)			
Os–C(1)	2.066(4)	Os–P(1)	2.341(1)
Os–P(2)	2.350(1)	C(1)–C(2)	1.158(5)
C(2)–C(3)	1.470(5)		
Bond angles (°)			
C(1)–Os–P(1)	86.08(11)	C(1)–Os–P(1')	93.92(11)
C(1)–Os–P(2)	81.51(10)	C(1)–Os–P(2')	98.49(10)
P(1)–Os–P(2)	70.15(4)	P(1)–Os–P(2')	109.85(4)
C(1)–Os–C(1')	180.0	P(1)–Os–P(1')	180.0
P(2)–Os–P(2')	180.0	C(2)–C(1)–Os	177.6(3)
C(1)–C(2)–C(3)	174.1(4)		

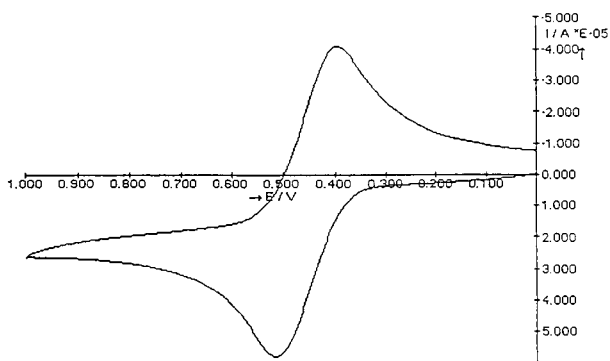


Fig. 5. Cyclic voltammogram of $[(\text{dppm})_2\text{Ru}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-CH}_3)]$ **10**.

osmium–ethyne bond (2.066(4) Å) is typical of a metal to conjugated carbon centre linkage. The ethyne C≡C bond distance of 1.158(5) Å is noticeably shorter than that observed in the ruthenium dinitro analogue [10b] and reflects a greater retention of triple bond character. Departures from linearity in the Os–C≡C–Ar linkages are small, being 177.6(3)° at C(1), and 174.1(4)° at C(2), respectively. As **12** is effectively isomorphous with the ruthenium dinitro and nitro/phenyl species, the packing of the molecules is essentially the same, there being no intermolecular contacts of note.

2.4. Electrochemistry of Ru(II) acetylides

The electron transfer process for the Ru^{II/III} redox couple in each complex was found to be quasi-reversible ($\Delta E_p = 60\text{--}100$ mV and $i_{pa}/i_{pc} = \text{ca. } 1$) (Fig. 5). The shift in the relative electrode potentials ($E_{1/2}$ std) were related to the change in electron density at the metal centre. These electrochemical data are consistent with previous published findings [12b] for $[(\text{C}_5\text{H}_5)\text{Ru}(\text{PR}_3)(\text{C}\equiv\text{CR}')] (R = \text{CH}_3, \text{C}_6\text{H}_5; R' = \text{C}_6\text{H}_5, \text{NO}_2)$ where electron density on the metal centre depends on the electron-withdrawing and -donating abilities of the acetylenic ligands. We have previously observed that the oxidation potential is reduced when chloride is replaced by electron donating ferrocenyl fragments [14]. A comparison of the $E_{1/2}$ std of the complexes $\text{trans}-[(\text{dppm})_2\text{RuCl}_2]$ and $\text{trans}-[(\text{dppm})_2\text{Ru}(\text{Cl})(\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)]$ showed that the Ru^{II/III} redox couple was stabilised by ca. 0.20 V towards oxidation for the latter (Table 7). This suggests that the acetylide ligand is more electron donating than the chloride. A comparison of the $E_{1/2}$ std values of the analogous $\text{trans}-[(\text{dppe})_2\text{RuCl}_2]$ and $\text{trans}-[(\text{dppe})_2\text{Ru}(\text{Cl})(\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)]$ complexes indicated a lower degree of stabilisation (0.07 V) by the (C≡C–Ph) ligand. This suggested that the donation/with-

drawal of electron density at a metal centre is a synergistic interaction and depends on all the ligands coordinated to the metal centre. Replacement of the chloride in complexes $\text{trans}-[(\text{dppm})_2\text{RuCl}_2]$ and $\text{trans}-[(\text{dppe})_2\text{RuCl}_2]$ by a (C≡C–C₆H₄-*p*-NO₂) ligand caused an increase in the $E_{1/2}$ std values by 0.04, and 0.14 V, respectively, and indicates that the Ru^{II/III} centre in both complexes is destabilised towards oxidation by the Cl[−] substitution as the –C≡C–C₆H₄-*p*-NO₂ species is a more electron withdrawing unit than Cl[−]. The relative destabilisation was again different in both complexes suggesting that the electron density at the metal centre depends on the coordinated phosphine ligands. Substitution of the remaining chloride of $\text{trans}-[(\text{dppm})_2\text{Ru}(\text{Cl})(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-NO}_2)]$ by an electron donor acetylide to give **7**, stabilised the ruthenium centre towards oxidation. Destabilisation of the metal centre was observed when the chloride was substituted by electron accepting nitro-acetylide to form **9**. The electrochemical data in Table 7 demonstrate the extent by which the electron density can change on going from a *trans*-dichloride [L₂RuCl₂] to a *trans*-bis-acetylide [L₂Ru(C≡C–R)₂]. For the $[(\text{dppm})_2\text{Ru}(\text{C}\equiv\text{C}-\text{R})_2]$ and $[(\text{dppe})_2\text{Ru}(\text{C}\equiv\text{C}-\text{R})_2]$ systems, the range of $E_{1/2}$ std values are 0.24 and 0.25 V, respectively. These results suggest that the systems can be fine-tuned to have particular electrochemical properties.

Table 7

Electrode potentials of some ruthenium(II) mono- and bis-acetylides

Complex	ΔE_p (mV)	$E_{1/2}$ std ^a (V)
$\text{trans}-[(\text{dppm})_2\text{RuCl}_2]$	70	0.09
$\text{trans}-[(\text{dppm})_2\text{Ru}(\text{Cl})(\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)]$	80	−0.112
$\text{trans}-[(\text{dppm})_2\text{Ru}(\text{Cl})(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-NO}_2)]$	75	0.13
$\text{trans}-[(\text{dppm})_2\text{Ru}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-NO}_2)(\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)]$ 7	80	0.02
$\text{trans}-[(\text{dppm})_2\text{Ru}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-NO}_2)(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-CH}_3)]$ 8	80	−0.01
$\text{trans}-[(\text{dppm})_2\text{Ru}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-NO}_2)_2]$ 9	70	0.17
$\text{trans}-[(\text{dppm})_2\text{Ru}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-CH}_3)]$ 10	100	−0.15
$\text{trans}-[(\text{dppe})_2\text{RuCl}_2]$	95	0.02
$\text{trans}-[(\text{dppe})_2\text{Ru}(\text{Cl})(\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)]$	80	−0.05
$\text{trans}-[(\text{dppe})_2\text{Ru}(\text{Cl})(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-NO}_2)]$ 3	90	0.16
$\text{trans}-[(\text{dppe})_2\text{Ru}(\text{Cl})(\text{C}\equiv\text{C}-\text{C}_6\text{H}_3\text{-}o\text{-CH}_3\text{-}p\text{-NO}_2)]$ 4	83	0.16
$\text{trans}-[(\text{dppe})_2\text{Ru}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-CH}_3)_2]$ 5	80	−0.09
$\text{trans}-[(\text{dppe})_2\text{Ru}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-NO}_2)_2]$ 6	61	0.23
$\text{trans}-[(\text{dppe})_2\text{Ru}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-NO}_2)]$	80	0.08
$\text{trans}-[(\text{dppe})_2\text{Ru}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)_2]$	80	−0.03

^a Scan rate 100 mVs^{−1}. All $E_{1/2}$ values referenced to ferrocene in the same system.

3. Experimental

3.1. General

All experiments were performed under nitrogen using standard Schlenk line techniques. Solvents were predried and distilled from appropriate drying agents. Solution IR spectra were recorded on a Perkin–Elmer 1710 Fourier-Transform IR spectrometer. The NMR spectra were recorded on a Bruker AM-400 spectrometer. The $^3\text{P}\{^1\text{H}\}$ -NMR chemical shifts are reported downfield from an external trimethylphosphite standard. Microanalyses were carried out in the Department of Chemistry, University of Cambridge and FAB (+ve ion) mass spectra were recorded using a Kratos MS60 spectrometer. The electrochemical investigations of the $\text{Ru}^{\text{II/III}}$ redox couple in complexes $\text{trans}-[\text{L}_2\text{RuR}_2]$ {where L = dpmm, dppe} were recorded at 298 K in a standard three-electrode system (platinum working/auxiliary electrodes and silver wire as pseudo reference electrode) using a 0.1 M $[\text{NBu}_4][\text{BF}_4]/\text{CH}_2\text{Cl}_2$ solution as electrolyte ($E_c = 0.47$ V vs. Ag/Ag^+ at 298 K in 0.1 M $[\text{NBu}_4][\text{BF}_4]/\text{CH}_2\text{Cl}_2$). The metal salts $\text{cis}-[(\text{dpmm})_2\text{MCl}_2]$ (M = Ru, Os) and $\text{trans}-[(\text{dppe})_2\text{RuCl}_2]$ and the alkynes were prepared by published procedures [15,16], as were the mono-acetylide complexes $\text{trans}-[(\text{dpmm})_2\text{M}(\text{Cl})(\text{C}\equiv\text{C}-\text{R})]$ (M = Ru, Os) [7e] and bis-acetylides $\text{trans}-[(\text{dpmm})_2\text{M}(\text{C}\equiv\text{C}-\text{Ph})_2]$ [6j] and $\text{trans}-[(\text{dppe})_2\text{Ru}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)(\text{C}\equiv\text{CC}_6\text{H}_4\text{-}p\text{-NO}_2)]$ [9d].

3.2. Syntheses

3.2.1. Mono-acetylides of $\{(\text{dppe})_2\text{Ru}(\text{II})\text{Cl}\}$

The mono-acetylide complexes were prepared by an adaptation of the procedure [9d]. To a CH_2Cl_2 solution of the metal chloride, $\text{trans}-[(\text{dppe})_2\text{RuCl}_2]$, three equivalents of the alkyne and three equivalents of NaPF_6 were added. The mixture was stirred for 5–7 days at r.t. The solution was filtered and the solvent was removed in vacuo. The sticky solid was washed three times with hexane (10 ml) to remove excess ligand and was then redissolved in CH_2Cl_2 (20 ml) and treated with one equivalent of DBU for 3 h. The solvent was then removed in vacuo and the complexes were purified by washing the crude solid with acetone (2×5 ml) and recrystallised from hexane:dichloromethane (1:1) to yield microcrystalline solids.

3.2.2. $\text{trans}-[(\text{dppe})_2\text{Ru}(\text{Cl})(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-CH}_3)]$ **1**

From the reaction of $\text{trans}-[(\text{dppe})_2\text{RuCl}_2]$ (0.29 g, 0.3 mmol), $\text{HC}\equiv\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-CH}_3$ (0.104 g, 0.9 mmol) and NaPF_6 (0.151 g, 0.9 mmol), 0.210 g (67%) of **1** was isolated. (Found: C, 69.91; H, 5.33. $\text{C}_{61}\text{H}_{55}\text{ClP}_4\text{Ru}$ requires C, 69.88; H, 5.29%; ν cm^{-1}

(CH_2Cl_2) 2074 ($\text{C}\equiv\text{C}$); δ_{H} (CDCl_3 , 250 Hz) 2.28 (s, 3H, CH_3), 2.6 (m, 8H, $\text{PCH}_2\text{CH}_2\text{P}$), 6.57 (d, $^3J(\text{H}^3-\text{H}^2)$ 8 Hz, 2H, H^3), H^2 protons overlap with diphos. aromatic protons, 6.90–7.40 (m, 40H, C_6H_5); $^3\text{P}\{^1\text{H}\}$ (CDCl_3 , 250 Hz) -91.3 ; m/z 1048.2 (M^+) 1047.5.

3.2.3. $\text{trans}-[(\text{dppe})_2\text{Ru}(\text{Cl})(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-C}_6\text{H}_5)]$ **2**

From the reaction of $\text{trans}-[(\text{dppe})_2\text{RuCl}_2]$ (0.29 g, 0.3 mmol), $\text{HC}\equiv\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-C}_6\text{H}_5$ (0.160 g, 0.9 mmol) and NaPF_6 (0.151 g, 0.9 mmol), 0.253 g (76%) of **2** was isolated. (Found: C, 71.41; H, 5.14. $\text{C}_{66}\text{H}_{57}\text{ClP}_4\text{Ru}$ requires C, 71.38; H, 5.17%; ν cm^{-1} (CH_2Cl_2) 2071 ($\text{C}\equiv\text{C}$); δ_{H} (CDCl_3 , 250 Hz) 2.6 (m, 8H, $\text{PCH}_2\text{CH}_2\text{P}$), 6.73 (d, $^3J(\text{H}^3-\text{H}^2)$ 8 Hz, 2H, H^3), H^2 protons overlap with diphos. aromatic protons, 6.95–7.47 (m, 47H, C_6H_5); $^3\text{P}\{^1\text{H}\}$ (CDCl_3 , 250 Hz) -91.3 ; m/z 1110 (M^+) 1110.

3.2.4. $\text{trans}-[(\text{dppe})_2\text{Ru}(\text{Cl})(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-NO}_2)]$ **3**

From the reaction of $\text{trans}-[(\text{dppe})_2\text{RuCl}_2]$ (0.29 g, 0.3 mmol), $\text{HC}\equiv\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-NO}_2$ (0.132 g, 0.9 mmol) and NaPF_6 (0.151 g, 0.9 mmol), 0.239 g (74%) of **3** was isolated. (Found: C, 65.28; H, 5.03. $\text{C}_{60}\text{H}_{52}\text{ClNO}_2\text{P}_4\text{Ru} \cdot \text{CH}_2\text{Cl}_2$ requires C, 64.77; H, 4.73%; ν cm^{-1} (CH_2Cl_2) 2051 ($\text{C}\equiv\text{C}$); δ_{H} (CDCl_3 , 250 Hz) 2.6 (m, 8H, $\text{PCH}_2\text{CH}_2\text{P}$), 6.43 (d, $^3J(\text{H}^3-\text{H}^2)$ 9 Hz, 2H, H^2), 7.93 (d, $^3J(\text{H}^2-\text{H}^3)$ 9 Hz, 2H, H^3), 6.80–7.30 (m, 40H, C_6H_5); $^3\text{P}\{^1\text{H}\}$ (CDCl_3 , 250 Hz) -92.5 ; m/z 1079 (M^+) 1079.

3.2.5. $\text{trans}-[(\text{dppe})_2\text{Ru}(\text{Cl})(\text{C}\equiv\text{C}-\text{C}_6\text{H}_3\text{-}o\text{-CH}_3\text{-}p\text{-NO}_2)]$ **4**

From the reaction of $\text{trans}-[(\text{dppe})_2\text{RuCl}_2]$ (0.29 g, 0.3 mmol), $\text{HC}\equiv\text{C}-\text{C}_6\text{H}_3\text{-}o\text{-CH}_3\text{-}p\text{-NO}_2$ (0.145 g, 0.9 mmol) and NaPF_6 (0.151 g, 0.9 mmol), 0.235 g (72%) of **4** was isolated. (Found: C, 66.49; H, 4.98. $\text{C}_{61}\text{H}_{54}\text{ClNO}_2\text{P}_4\text{Ru}$ requires C, 66.94; H, 4.93%; ν cm^{-1} (CH_2Cl_2) 2029 ($\text{C}\equiv\text{C}$); δ_{H} (CDCl_3 , 250 Hz) 1.6 (s, 3H, CH_3), 2.6 (m, 4H, $\text{PCH}_2\text{CH}_2\text{P}$), 2.8 (m, 4H, $\text{PCH}_2\text{CH}_2\text{P}$), 6.54 (d, $^3J(\text{H}^3-\text{H}^2)$ 8.5 Hz, 1H, H^2), 7.84 (d, $^4J(\text{H}^3-\text{H}^5)$ 2.25 Hz, 1H, H^5), 6.80–7.20 (m, 41H, C_6H_5); $^3\text{P}\{^1\text{H}\}$ (CDCl_3 , 250 Hz) -91.8 ; m/z 1094 (M^+) 1093.5.

3.2.6. $\text{trans}-[(\text{dppe})_2\text{Ru}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-CH}_3)_2]$ **5**

This was prepared by following a method from our earlier report [6j]. A mixture of $\text{Me}_3\text{SnC}\equiv\text{C}-\text{C}_6\text{H}_5$ (0.05 g, 0.05 mmol), $\text{trans}-[(\text{dppe})_2\text{RuCl}_2]$ (0.41 g, 0.15 mmol) and CuI (3 mg) in CH_2Cl_2 (25 ml) was refluxed for 24 h under inert atmosphere. The solution was allowed to come to r.t. and the volume was reduced to 5 ml and applied to a short neutral grade II alumina column. Eluting the column with dichloromethane resulted in a yellow solution which was evaporated to dryness to afford a bright yellow

product. Yield: 0.038 g, 65%; (Found: C, 74.15; H, 5.79. $C_{70}H_{62}P_4Ru$ requires C, 74.52; H, 5.54%); ν cm^{-1} (CH_2Cl_2) 2062 ($C\equiv C$); $^{31}P\{^1H\}$ ($CDCl_3$, 250 Hz) – 87.1.

3.2.7. *trans*-[(*dppe*)₂Ru($C\equiv C-C_6H_4-p-NO_2$)₂] **6**

This was prepared following a method reported by Miguel et al. [17]. $HC\equiv C-C_6H_4-p-NO_2$ (0.044 g, 0.3 mmol) and $AgBF_4$ (0.058 g, 0.3 mmol) were stirred for 20 min in a 3:1 mixture of dichloromethane and water (30 ml) in the absence of light. *trans*-[(*dppe*)₂RuCl₂] (0.097 g, 0.1 mmol) was added into the reaction mixture and stirred for another 20 h. The solution was filtered and the aqueous layer was removed. The organic layer was stirred with 1 M aqueous $Na_2S_2O_7$ for 0.5 h. It was then separated and dried over magnesium sulphate. After removal of the solvent under reduced pressure the crude product was purified by column chromatography on neutral grade II alumina using a 1:1 mixture of dichloromethane and hexane as eluent. Yield: 0.053 g, 45%; (Found: C, 68.64; H, 5.10. $C_{68}H_{56}N_2O_4P_4Ru$ requires C, 68.63; H, 4.74%); ν cm^{-1} (CH_2Cl_2) 2043 ($C\equiv C$); δ_H ($CDCl_3$, 250 Hz) 2.6 (m, 8H, PCH_2CH_2P), 6.64 (d, $^3J(H^3-H^2)$ 9 Hz, 4H, H^2), 7.99 (d, $^3J(H^2-H^3)$ 9 Hz, 4H, H^3), 6.83–7.40 (m, 40H, C_6H_5); $^{31}P\{^1H\}$ ($CDCl_3$, 250 Hz) – 88.2.

3.3. Unsymmetrical bis-acetylides of Ru(II) and Os(II)

The unsymmetrical σ -acetylide complexes featuring *dpmm* as chelating ligand were prepared by following a general procedure outlined below for complex **7**.

3.3.1. *trans*-[(*dpmm*)₂Ru($C\equiv C-C_6H_5$)($C\equiv CC_6H_4-p-NO_2$)] **7** and *trans*-[(*dpmm*)₂Ru($C\equiv C-C_6H_4-p-NO_2$)₂] **9**

To a solution of *trans*-[(*dpmm*)₂Ru(Cl)($C\equiv C-C_6H_4-p-NO_2$)] (0.21 g, 0.2 mmol) in THF (20 ml), $Me_3SnC\equiv C-C_6H_5$ (0.58 g, 0.11 mmol) and CuI (3 mg) were added. The reaction mixture was stirred for 3 h under reflux. The solvent was then evaporated to dryness in vacuo and the residue was purified by column chromatography on neutral grade II alumina using a 1:1 mixture of dichloromethane and hexane as eluent. The first red band was identified as *trans*-[(*dpmm*)₂Ru($C\equiv C-C_6H_5$)($C\equiv CC_6H_4-p-NO_2$)] (**7**) in 49% yield (0.11 g); (Found: C, 70.66; H, 4.84. $C_{66}H_{53}NO_2P_4Ru$ requires C, 70.97; H, 4.74%); ν cm^{-1} (CH_2Cl_2) 2054, 2079 ($C\equiv C$); δ_H ($CDCl_3$, 250 Hz) 4.82 (m, 4H, PCH_2P), 6.09 (d, $^3J(H^3-H^2)$ 9 Hz, 2H, H^2), 7.78 (d, $^3J(H^2-H^3)$ 9 Hz, 2H, H^3), 6.83–7.47 (m, 45H, C_6H_5); $^{31}P\{^1H\}$ ($CDCl_3$, 250 Hz) – 144.9; m/z 1116 (M^+) 1116; and the second band as *trans*-[(*dpmm*)₂Ru($C\equiv CC_6H_4-p-NO_2$)₂] (**9**) in 17% yield (0.04 g); (Found: C, 67.71; H, 4.40. $C_{66}H_{52}N_2O_2P_4Ru$ requires C, 68.21; H, 4.47%); ν cm^{-1} (CH_2Cl_2) 2052 ($C\equiv C$); δ_H ($CDCl_3$, 250 Hz) 4.85 (m, 4H, PCH_2P), 6.13 (d, $^3J(H^3-H^2)$ 9 Hz, 4H, H^2), 7.80 (d,

$^3J(H^2-H^3)$ 9 Hz, 4H, H^3), 6.84–7.66 (m, 40H, C_6H_5); $^{31}P\{^1H\}$ ($CDCl_3$, 250 Hz) – 145.2; m/z 1162 (M^+) 1161.

3.3.2. *trans*-[(*dpmm*)₂Ru($C\equiv C-C_6H_4-p-NO_2$)-($C\equiv CC_6H_4-p-CH_3$)] **8**

From the reaction of *trans*-[(*dpmm*)₂Ru(Cl)($C\equiv C-C_6H_4-p-NO_2$)] (0.210 g, 0.2 mmol), $Me_3SnC\equiv C-C_6H_4-p-CH_3$ (0.061 g, 0.22 mmol) and CuI (5 mg), 0.106 g (45%) of **8** was isolated (along with 0.018 g of **9** (8 %)). (Found: C, 71.20; H, 4.98. $C_{67}H_{55}NO_2P_4Ru$ requires C, 71.15; H, 4.86%); ν cm^{-1} (CH_2Cl_2) 2054, 2080 ($C\equiv C$); δ_H ($CDCl_3$, 250 Hz) 2.22 (s, 3H, CH_3), 4.83 (m, 4H, PCH_2P), 6.08 (d, $^3J(H^3-H^2)$ 9 Hz, 2H, H^2), 7.77 (d, $^3J(H^2-H^3)$ 9 Hz, 2H, H^3), 6.08 (d, $^3J(H^7-H^8)$ 8 Hz, 2H, H^7), 7.77 (d, $^3J(H^7-H^8)$ 8 Hz, 2H, H^8), 6.84–7.66 (m, 40H, C_6H_5); $^{31}P\{^1H\}$ ($CDCl_3$, 250 Hz) – 145.0; m/z 1131 (M^+) 1130.

3.3.3. *trans*-[(*dpmm*)₂Ru($C\equiv C-C_6H_5$)($C\equiv CC_6H_4-p-CH_3$)] **10**

From the reaction of *trans*-[(*dpmm*)₂Ru(Cl)($C\equiv C-C_6H_5$)] (0.201 g, 0.2 mmol), $Me_3SnC\equiv C-C_6H_4-p-CH_3$ (0.061 g, 0.22 mmol) and CuI (5 mg), 0.099 g (46%) of **10** was isolated. (Found: C, 73.73; H, 5.16. $C_{67}H_{56}P_4Ru$ requires C, 74.10; H, 5.16%); ν cm^{-1} (CH_2Cl_2) 2069 ($C\equiv C$); δ_H ($CDCl_3$, 250 Hz) 2.21 (s, 3H, CH_3), 4.83 (m, 4H, PCH_2P), 6.20 (d, $^3J(H^3-H^2)$ 8 Hz, 2H, H^2), 7.75 (d, $^3J(H^2-H^3)$ 8 Hz, 2H, H^3), 6.76–7.79 (m, 45H, C_6H_5); $^{31}P\{^1H\}$ ($CDCl_3$, 250 Hz) – 144.6; m/z 1083 (M^+) 1085.

All the unsymmetrical bis-acetylide complexes of osmium were synthesised using the general procedure of stirring *trans*-[(*dpmm*)₂OsCl($C\equiv C-C_6H_4-R$)] with $Me_3SnC\equiv C-R$ in THF in the presence of CuI for 20 h under reflux.

3.3.4. *trans*-[(*dpmm*)₂Os($C\equiv C-C_6H_4-p-NO_2$)-($C\equiv C-C_6H_5$)] **11**

From the reaction of *trans*-[(*dpmm*)₂Os(Cl)($C\equiv C-C_6H_4-p-NO_2$)] (0.341 g, 0.33 mmol), $Me_3SnC\equiv C-C_6H_5$ (0.087 g, 0.33 mmol) and CuI (7 mg), 0.107 g (30%) of **11** was isolated. (Found: C, 62.48; H, 4.09. $C_{66}H_{53}NO_2P_4Os$. CH_2Cl_2 requires C, 62.32; H, 4.26%); ν cm^{-1} (CH_2Cl_2) 2052, 2080 ($C\equiv C$); δ_H ($CDCl_3$, 250 Hz) 5.40 (m, 4H, PCH_2P), 6.02 (d, $^3J(H^3-H^2)$ 9 Hz, 2H, H^2), 7.78 (d, $^3J(H^2-H^3)$ 9 Hz, 2H, H^3), 6.83–7.43 (m, 45H, C_6H_5); $^{31}P\{^1H\}$ ($CDCl_3$, 250 Hz) – 191.4; m/z 1209 (M^+) 1207.

3.3.5. *trans*-[(*dpmm*)₂Os($C\equiv C-C_6H_4-p-NO_2$)($C\equiv C-C_6H_4-p-CH_3$)] **12**

From the reaction of *trans*-[(*dpmm*)₂Os(Cl)($C\equiv C-C_6H_4-p-NO_2$)] (0.113 g, 0.1 mmol), $Me_3SnC\equiv C-C_6H_4-p-CH_3$ (0.030 g, 0.11 mmol) and CuI (5 mg), 0.032 g (27%) of **12** was isolated. (Found: C, 62.40; H, 4.23. $C_{67}H_{55}NO_2P_4Os$. CH_2Cl_2 requires C, 62.58; H, 4.37%); ν

Table 8
Crystal data and structure refinement parameters^a

Data	3	4	12
Empirical formula	C ₆₀ H ₅₂ NO ₂ P ₄ ClRu	C ₆₁ H ₅₄ NO ₂ P ₄ ClRu	C ₆₇ H ₅₅ NO ₂ P ₄ Os
Solvent	CH ₂ Cl ₂	–	–
Formula weight	1164.4	1093.5	1220.2
Colour, habit	Yellow block	Red block	Deep red plate
Crystal size (mm)	0.30 × 0.10 × 0.10	0.18 × 0.13 × 0.08	0.26 × 0.08 × 0.04
Lattice type	Triclinic	monoclinic	Triclinic
Space group	<i>P</i> $\bar{1}$, 2	<i>P</i> 2 ₁ / <i>n</i> , 14	<i>P</i> $\bar{1}$, 2
Temperature (K)	153	290	293
Unit cell dimensions			
<i>a</i> (Å)	13.910(3)	13.478(3)	9.808(2)
<i>b</i> (Å)	17.301(3)	16.105(3)	12.456(3)
<i>c</i> (Å)	13.685(3)	24.088(5)	12.760(4)
α (°)	108.97(3)	–	80.93(2)
β (°)	119.41(3)	90.61(3)	68.40(2)
γ (°)	90.28(3)	–	72.24(2)
<i>V</i> (Å ³)	2658.5(9)	5228(2)	1378.6(6)
<i>Z</i>	2	4	1 ^b
<i>D</i> _{calc.} (g cm ⁻³)	1.455	1.389	1.470
<i>F</i> (000)	1196	2256	616
Diffractometer	Rigaku AFC7	Rigaku AFC5R	Siemens P4/PC
Radiation used	Mo–K α	Mo–K α	Cu–K α
μ (mm ⁻¹)	0.61	0.52	5.83
Theta range for data collection (°)	2.5–22.5	2.5–22.5	3.7–63.0
Scan type	$\omega/2\theta$	$\omega/2\theta$	ω
Reflections collected	6923	6839	4462
Reflections observed $ F_0 > 4\sigma(F_0)$	5598	2919	4396
Absorption correction	Semi-empirical	Semi-empirical	Gaussian
Max./min. transmission	1.00, 0.94	1.00, 0.87	0.80, 0.41
No. of variables	553	535	302
<i>R</i> ₁ ^c	0.052	0.072	0.029
<i>wR</i> ₂ ^d	0.142	0.134	0.074
Weighting factors <i>a</i> , <i>b</i> ^e	0.112, 0.000	0.055, 0.000	0.039, 1.972
Largest difference peak and hole (e Å ⁻³)	1.16, –1.72	0.79, –0.57	0.56, –1.08

^a Details in common: graphite monochromated radiation, refinement based on *F*².

^b The molecule is disordered about a crystallographic centre of symmetry, see text.

^c $R_1 = \frac{\sum ||F_0| - |F_c||}{\sum |F_0|}$.

^d $wR_2 = \sqrt{\frac{\sum [w(F_0^2 - F_c^2)]^2}{\sum [w(F_0^2)]^2}}$.

^e $w^{-1} = \sigma^2(F_0^2) + (aP)^2 + bP$.

cm⁻¹ (CH₂Cl₂) 2051, 2083 (C≡C); δ_H (CDCl₃, 250 Hz) 2.22 (s, 3H, CH₃), 4.83 (m, 4H, PCH₂P), acetylide aromatic protons were not clearly observed, 6.76–7.79 (m, 48H, C₆H₅); ³¹P{¹H} (CDCl₃, 250 Hz) –191.4; *m/z* 1218 (*M*⁺) 1220.

3.3.6. *trans*-[(*dppm*)₂Os(C≡C–C₆H₅)(C≡C–C₆H₄–*p*-CH₃)] **13**

From the reaction of *trans*-[(*dppm*)₂Os(Cl)(C≡C–C₆H₅)] (0.109 g, 0.1 mmol), Me₃SnC≡C–C₆H₄–*p*-CH₃ (0.030 g, 0.11 mmol) and CuI (5 mg), 0.034 g (29%) of **13** was isolated. (Found: C, 67.07; H, 4.73. C₆₇H₅₆P₄Os.0.5CH₂Cl₂ requires C, 66.69; H, 4.69%); ν cm⁻¹ (CH₂Cl₂) 2069 (C≡C); δ_H (CDCl₃, 250 Hz) 2.30 (s, 3H, CH₃), 5.39 (m, 4H, PCH₂P) 6.28 (d, ³J(H²-H³) 9 Hz, 4H, H²), 6.90 (d, ³J(H²-H³) 9 Hz, 4H, H³), 7.02–7.66 (m, 41H, C₆H₅); ³¹P{¹H} (CDCl₃, 250 Hz) –195.0; *m/z* 1178 (*M*⁺) 1175.

4. Crystallography

Table 8 provides a summary of the crystal data, data collection and refinement parameters for complexes **3**, **4** and **12**. All three structures were solved by the heavy atom method and all the non-hydrogen atoms were refined anisotropically by full matrix least-squares based on *F*². In each structure all the pendant phenyl rings were refined as idealised rigid bodies. In **4** and **12** the hydrogen atoms of the methyl groups attached to sp² centres were located from a ΔF map, idealised, assigned isotropic thermal parameters, *U*(H) = 1.5 *U*_{eq}(C), and allowed to ride on their parent atoms. The remaining hydrogen atoms in all three structures were placed in calculated positions, assigned isotropic thermal parameters, *U*(H) = 1.2 *U*_{eq}(C), and allowed to ride on their parent atoms. Computations were carried out using the SHELXTL PC program system [18].

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 116212 and 115337 for compounds **3** and **12**, respectively. Compound **4** can be found on the CCDC Database under code NABBEX. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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