

Synthetic and electrochemical studies of some metal complexes of 1,3,5-triethynylbenzene

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A series of compounds featuring metallic fragments around the periphery of a 1,3,5-triethynylbenzene core have been synthesized. By using several synthetic methods, metallic units such as *cis*-[RuCl₂(dppm)₂], *cis*-[OsCl₂(dppm)₂] and [RuCl(η-C₅H₅)(PPh₃)₂] have been treated with the aromatic acetylide ligand to introduce one, two or three metallic centres. Electrochemical studies showed that the bimetallic *trans*-[HC≡CC₆H₃{C≡CRuCl(dppm)₂}₂] and *trans*-[HC≡CC₆H₃{C≡COsCl(dppm)₂}₂] species undergo two separated one-electron oxidations thus indicating that the central triethynylbenzene unit allows communication between the two peripheral metal subunits. The compounds [(HC≡C)₂C₆H₃C≡CRu(η-C₅H₅)(PPh₃)₂], [HC≡CC₆H₃{C≡CRu(η-C₅H₅)(PPh₃)₂}₂] and [C₆H₃{C≡CRu(η-C₅H₅)(PPh₃)₂}₃] each show separated one-electron oxidations (though these are less reversible than for the previous compounds mentioned) again demonstrating the electronic communication amongst the peripheral metal centres through the organic linkage. Chemical oxidation has been carried out on the [Ru(η-C₅H₅)(PPh₃)₂]-containing species affording mixed-valence species consistent with those produced by successive electrochemical oxidation.

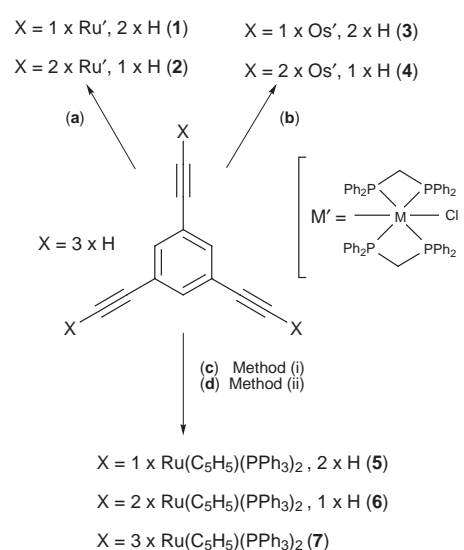
Carbon-rich organometallics containing rigid π-conjugated chains are of increasing interest due to their uses in the syntheses of unsaturated organic species,¹ organometallic polymers² and π-conjugated bi- or multi-metallic systems.³ A central triethynylbenzene core is of particular interest due to its geometry and its active co-ordination sites. This 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-C₅Me₅)(dpppe)],⁵ [IrCl(PPh₃)₂(CO)(MeCN)],⁶ [Cr(η-C₆H₆)(CO)₃],⁷ [Ru(bpy)₂(phen)]²⁺,⁸ [Au(PR₃)₃]⁹ and [PtCl(XBuⁿ)₃]₂ (X = P or As)^{3h} around the periphery of the organic ligand, in order to probe the ability of the metal to participate in π delocalisation, as well as the potential for interaction of the metal d orbitals with the conjugated π orbitals of the organic moiety.

In particular, metal acetylide complexes have attracted interest as precursors to molecules containing delocalised π systems and additionally allow communication between co-ordinated metal centres.¹⁰ These studies aim to exploit the electronic- and photonic-based co-operation between individual transition metal subunits of a molecular assembly having a delocalised π backbone and the complexes are predicted to find applications in the areas of molecular devices,¹¹ organometallic polymers,^{2,12} non-linear optics¹³ and molecular electronics.^{11,14,15} Utilisation here of the reaction of terminal alkynes with halide-bearing metal complexes *via* several synthetic routes has resulted in the isolation and characterisation of seven new compounds. The complexes discussed herein form a series of novel precursors for the production of metal–aromatic polyyne networks.

Results and Discussion

Synthesis

The multinuclear σ-acetylide complexes synthesized were of the type (XC≡C)₃C₆H₃ {X = H, *trans*-[RuCl(dppm)₂], *trans*-[OsCl(dppm)₂] or [Ru(η-C₅H₅)(PPh₃)₂]} using the versatile starting material 1,3,5-triethynylbenzene and the relevant metal fragments (Scheme 1). A high level of purity of the starting materials ensured that the yellow, microcrystalline products



Scheme 1 Synthesis of complexes 1–7. (a) CH₂Cl₂, *cis*-[RuCl₂(dppm)₂], NaPF₆, 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu); (b) CH₂Cl₂, *cis*-[OsCl₂(dppm)₂], NaPF₆, dbu; (c) method (i) CH₂Cl₂, NH₄PF₆, [RuCl(η-C₅H₅)(PPh₃)₂], dbu; (d) method (ii) MeOH, [RuCl(η-C₅H₅)(PPh₃)₂], reflux, Na

were isolated in reasonable to good yields, depending on the synthetic method employed. All efforts to produce X-ray quality crystals failed due to the instability of the products in solution over prolonged periods.

For the *trans*-[MCl(dppm)₂] complexes the preferred synthetic method was one elucidated by Dixneuf and co-workers,^{10j} modified in the Experimental section. Importantly, the dichlorides used offer two reactive sites and therefore have potential to form oligomeric and polymeric structures^{10b} based around a trisubstituted benzene unit. The monosubstituted species, *trans*-[(HC≡C)₂C₆H₃C≡CRu(dppm)₂Cl] **1** and *trans*-[(HC≡C)₂C₆H₃C≡COs(dppm)₂Cl] **3** were formed in good yields of 63% and 50% respectively with the 1:1 stoichiometry of reactants reducing the number of possible by-products and side reactions. The reaction times of 4 (Ru) and 8 h (Os) were relatively

short in comparison to those for the disubstituted species *trans*-[HC≡CC₆H₃{C≡CRu(dppm)₂Cl}₂] **2** and *trans*-[HC≡CC₆H₃{C≡COs(dppm)₂Cl}₂] **4** which featured reaction times of *ca.* 24 h and lower yields of 20 (Ru) and 30% (Os). This may be accounted for by cross-coupling reactions of the starting materials (facilitated by longer reaction times) or by the instability of intermediates or products in solution. Surprisingly, all attempts to form the trisubstituted metal acetylide species were unsuccessful using these methods and instead resulted in the isolation of the disubstituted species with reduced yields and purity.

The mono-, di- and tri-substituted species, [(HC≡C)₂-C₆H₃C≡CRu(η-C₅H₅)(PPh₃)₂] **5**, [HC≡CC₆H₃{C≡CRu(η-C₅H₅)(PPh₃)₂}₂] [PF₆]₂ **6** and [C₆H₃{C≡CRu(η-C₅H₅)(PPh₃)₂}₃] **7**, respectively, were formed in good yields (60–66%) by the reaction of [RuCl(η-C₅H₅)(PPh₃)₂] with 1,3,5-triethynylbenzene in refluxing methanol followed by the addition of sodium metal. This methodology, adapted from that of Field *et al.*,^{3p} was preferred over the method illustrated above, as the latter only produced the mono- (**5**) and di-substituted (**6**) forms in low yields of 20 and 17% respectively. However, the method using sodium metal could not be employed to form complexes **1–4** as *both* chlorides would be activated encouraging the formation of species such as [(HC≡C)₂C₆H₃(C≡C)M(dppm)₂(C≡C)C₆H₃(C≡CH)₂] and higher nuclearity materials instead of the desired products. Chemical oxidation of **6** and **7** using ferrocenium hexafluorophosphate as oxidising agent in dry dichloromethane resulted in the isolation of [HC≡CC₆H₃{C≡CRu(η-C₅H₅)(PPh₃)₂}₂][PF₆]₂ **8** (after single oxidation of **6**), [C₆H₃{C≡CRu(η-C₅H₅)(PPh₃)₂}₃][PF₆]₂ **9** and [C₆H₃{C≡CRu(η-C₅H₅)(PPh₃)₂}₃][PF₆]₂ **10** (after single and double oxidations of **7** respectively). During the reactions an associated colour change was observed of yellow to dark green for all the mixed-valence species formed.

The complexes were characterised by IR and NMR spectroscopies. The IR spectra show a typical absorption for the carbon–carbon triple bond in the range 2063–2071 cm⁻¹ for **1–7** which represents a useful monitoring tool as there is a significant shift in frequency from the free alkyne [$\nu(\text{C}\equiv\text{C})$ 2114 cm⁻¹]. The C≡C stretching values are consistent with those observed for similar metal acetylide complexes^{4,5} and furthermore formation of the trinuclear species **7** could be followed to completion by disappearance of the C≡C–H band (3302 cm⁻¹). The IR spectra for the mixed-valence compounds **8–10** illustrated both the stretching frequencies for the oxidised [$\nu(\text{C}=\text{C})$] 1970–1980 cm⁻¹ and non-oxidised [$\nu(\text{C}\equiv\text{C})$] sites within the molecules.¹⁶

The ¹H NMR spectra (CDCl₃) of complexes **1–7** exhibit resonances characteristic of the CH₂ group in the bridging phosphine (δ 4.9), the acetylenic proton (when present) (δ 2.9) as well as a complicated series of multiplets for the aromatic protons of the phenyls present (δ 7.0–7.6). The ³¹P-¹H NMR of all the complexes showed a singlet indicative of equivalent phosphine environments and this is consistent with the *trans* geometry of the dppm ligands in **1–4** and of the equivalence of the PPh₃ ligands for **5–7**. The ¹H NMR spectra of **8–10** showed a significant broadening of the resonances detailed above, but the ³¹P-¹H NMR of each species showed two singlets indicative of the oxidised and non-oxidised sites at *ca.* δ 42.5 and 51.1 respectively as well as a septet centred at δ -143.6 characteristic of the counter anion PF₆⁻.

Electrochemistry

Fig. 1 shows the redox behaviour of complexes **1** and **2** in CH₂Cl₂ solution. In contrast to the precursor *cis*-[RuCl₂(dppm)₂], which exhibits an oxidation process followed by chemical complications,¹⁷ the oxidation of **1** involves a chemically and electrochemically reversible one-electron transfer. In fact, controlled potential coulometry ($E_w = +0.7$ V) consumes one electron per molecule and the resulting solution displays a cyclic voltammetric profile quite complementary to the original

Table 1 Formal electrode potentials (in V, vs. SCE) and peak-to-peak separations (in mV) exhibited by the triethynylbenzene complexes of Ru^{II} and Os^{II} and related species in CH₂Cl₂ solution

Complex	E°_{01+}	ΔE_p^a	E°_{02+}	ΔE_p^a	Ref.
<i>cis</i> -[RuCl ₂ (dppm) ₂]	+0.75	74			<i>b</i>
	+0.79	—			17
1	+0.41	81			<i>b</i>
2	+0.26	76	+0.46	76	<i>b</i>
1A	+0.49	90 ^c			10(g)
2A	+0.15	80 ^c	+0.51	80 ^c	10(g)
<i>cis</i> -[OsCl ₂ (dppm) ₂]	+0.60	64			<i>b</i>
	+0.64	—			17
3	+0.19	84			<i>b</i>
4	+0.05	59	+0.23	67	<i>b</i>
[Ru(η-C ₅ H ₅)(PPh ₃) ₂ Cl]	+0.52	109			<i>b</i>
	+0.60	—			19
5	+0.48	261 ^d			<i>b</i>
6	+0.32	<i>e</i>	+0.48	<i>e</i>	<i>b</i>
7 ^f	+0.22	<i>e</i>	+0.35	<i>e</i>	<i>b</i>

^a Measured at 0.2 V s⁻¹, in mV. ^b Present work. ^c Measured at 0.1 V s⁻¹.

^d Quasi-reversible process followed by irreversible chemical reactions.

^e Peak-to-peak separation not well defined. ^f $E^{\circ}_{03+} + 0.50$ V, see footnote *e*.

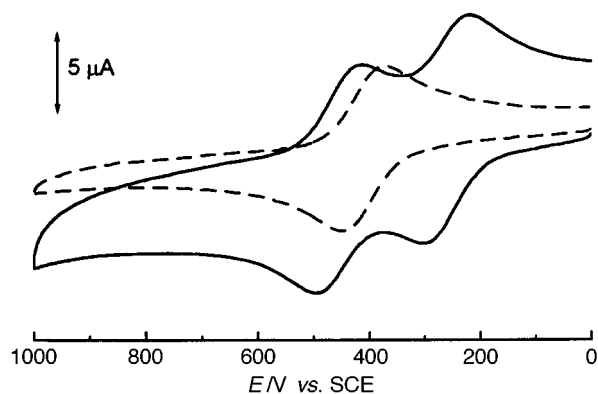


Fig. 1 Cyclic voltammetric responses recorded at a platinum electrode on a CH₂Cl₂ solution containing [NBu₄][PF₆] (0.2 M) and complexes **1** (6×10^{-4} M) (---) and **2** (6×10^{-4} M) (—). Scan rate 0.2 V s⁻¹

one; in addition, analysis¹⁸ of the cyclic voltammetric responses with scan rate varying from 0.02 to 1.00 V s⁻¹ shows that: (i) the $i_{pc}:i_{pa}$ ratio is equal to 1 : 1 throughout; (ii) the current function $i_{pa}/v^{1/2}$ remains virtually constant, decreasing by less than 10% for a ten-fold increase in scan rate; (iii) the peak-to-peak separation slightly increases from 70 to 90 mV. Upon exhaustive oxidation the original yellow solution turns green, and in the visible region displays a band at $\lambda_{max} = 597$ nm (absorption coefficient $\epsilon = 3.9 \times 10^3$ M⁻¹ cm⁻¹) and a broad band at $\lambda_{max} = 820$ nm (too broad to obtain the absorption coefficient), attributable to metal to ligand charge transfer.

Complex **2** displays two sequential one-electron oxidations, which are chemically and electrochemically reversible. Both the first exhaustive one-electron oxidation ($E_w = +0.35$ V) and the subsequent one ($E_w = +0.7$ V) turn the original yellow solution green. In both cases, similar bands to those cited above, at $\lambda_{max} = 596$ nm ($\epsilon = 4.7 \times 10^3$ M⁻¹ cm⁻¹) and 825 nm, are displayed. Owing to our spectrophotometric upper limit of 1100 nm we were unable to detect the likely presence of the charge transfer band of the mixed valent monocation [**2**]⁺. It must be taken into account that the larger the K_{com} (comproportionation constant = $16.9\Delta E_p$) value the higher is the wavelength of the intervalence charge transfer.¹⁵ The formal electrode potentials of all these redox changes are listed in Table 1. It is clear that replacing the one electron-withdrawing chlorine atom of *cis*-[RuCl₂(dppm)₂] with the triethynylbenzene fragment not only facilitates the Ru^{II}–Ru^{III} oxidation, indicating that it acts

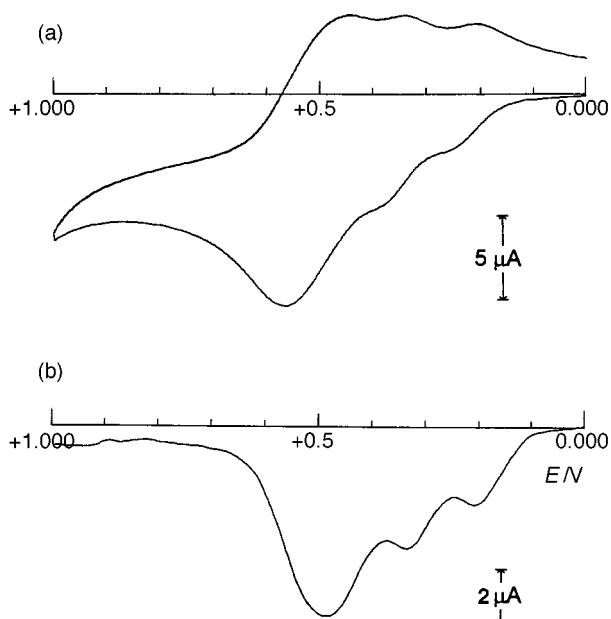


Fig. 2 Cyclic (a) and differential pulse (b) voltammetric responses recorded at a platinum electrode on a CH_2Cl_2 solution containing complex **7** (5×10^{-4} M) and $[\text{NBu}_4][\text{PF}_6]$ (0.2 M). Scan rates: (a) 0.2, (b) 0.004 V s^{-1}

as an electron donating group, but also results in a more stable ruthenium(III) species than that resulting from the oxidation of *cis*- $[\text{RuCl}_2(\text{dppm})_2]$. Similar behaviour was observed for the related 1,4-diethynylbenzene complexes $[\text{HC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CRu}(\text{dppe})_2\text{Cl}]$ **1A** and $[\text{Cl}(\text{dppe})_2\text{RuC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CRu}(\text{dppe})_2\text{Cl}]$ **2A**.^{10g} The fact that the diruthenium complex **2** exhibits two separated one-electron oxidations shows that the central triethynylbenzene units allow communication between the two peripheral ruthenium subunits. The separation between the two oxidation processes ($\Delta E^{or} = 0.20 \text{ V}$) allows a K_{com} of 2.4×10^3 to be calculated, which testifies that the mixed-valence $\text{Ru}^{\text{II}}\text{--Ru}^{\text{III}}$ monocation belongs to the slightly delocalised Robin-Day's Class II. It should be noted that the electronic communication between the two ruthenium centres through the triethynylbenzene unit is perhaps surprising in that we have recently found that complexes 1-bromo-3,5-bis(ethynylferrocenyl)benzene and 1,3,5-tris(ethynylferrocenyl)benzene undergo single-stepped two- and three-electron oxidations, respectively.⁴ This datum, however, is consistent with for example Dixneuf's observation that the communication between metal centres through a bridging unit is affected by the nature of either the bridge or the terminal metal fragments.^{10g}

The osmium analogues *cis*- $[\text{OsCl}_2(\text{dppm})_2]$ **3** and **4** show similar electrochemical responses to those discussed above for the ruthenium species except that, as previously reported,¹⁷ *cis*- $[\text{Os}^{\text{II}}\text{Cl}_2(\text{dppm})_2]$ undergoes a chemically reversible one-electron oxidation. Exhaustive oxidation of *cis*- $[\text{Os}^{\text{II}}\text{Cl}_2(\text{dppm})_2]$ to *cis*- $[\text{Os}^{\text{III}}\text{Cl}_2(\text{dppm})_2]^+$ turns the original yellow dichloromethane solution violet and displays a broad absorption band in the range from 510 to 750 nm. The electrochemical characteristics of the osmium complexes are included in Table 1. In agreement with previous findings on related species,^{17,20,21} the $\text{Os}^{\text{II}}\text{--Os}^{\text{III}}$ redox change is easier than the $\text{Ru}^{\text{II}}\text{--Ru}^{\text{III}}$ one. As far as the oxidation of complexes **3** and **4** is concerned, the green solutions of $[\mathbf{3}]^+$ and $[\mathbf{4}]^+$ exhibit absorption bands at $\lambda_{\text{max}} = 700$ and 710 nm respectively.

In agreement with a brief, preliminary report,¹⁹ $[\text{RuCl}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]$ undergoes a chemically reversible one-electron oxidation. The change from orange to pale orange which accompanies the electron removal causes a shoulder at 550 nm to appear in the original broad absorption located between 330 and 510 nm . The $\text{Ru}^{\text{II}}\text{--Ru}^{\text{III}}$ oxidation appears electrochemically quasi-reversible and suggests that some

significant structural reorganisation accompanies the electron removal. Progressive attachment of $\{\text{Ru}(\text{C}_5\text{H}_5)(\text{PPh}_3)_2\}$ fragments results in decreasing stability of the cations. In fact, **5** undergoes a one-electron oxidation followed by fast chemical complications. On the other hand, **6** and **7** undergo separated two- and three-electron oxidations respectively, which in cyclic voltammetry have features of chemical reversibility but in the longer times of controlled potential coulometry are followed by complete decomposition of the electrogenerated cations. As an example, Fig. 2 shows the electrochemical profile exhibited by **7**. This behaviour is rather reminiscent of that exhibited by the related tris- $\{\text{Fe}(\text{C}_5\text{H}_5)(\text{dppe})\}$ derivative,⁵ even if the latter exhibits fairly reversible $\text{Fe}^{\text{II}}\text{--Fe}^{\text{III}}$ oxidations, at least, on the cyclic voltammetric timescale. Despite the instability of complexes $[\mathbf{6}]^{2+}$ and $[\mathbf{7}]^{3+}$, as discussed above the appearance of separated one-electron oxidations is significant from the viewpoint of the electronic communication amongst the peripheral metal centres, when one considers that the tri(ethynylferrocene)-benzene analogues do not show communication between ferrocene subunits.⁴

Experimental

General

All preparations were carried out using standard Schlenk techniques.²² All solvents were distilled over standard drying agents under nitrogen directly before use and all reactions were carried out under an atmosphere of nitrogen.

All NMR spectra were recorded using a Delta upgrade on a JEOL 270 MHz spectrometer. Chemical shifts are reported in δ using CDCl_3 (^1H δ 7.25) as reference. Infrared spectra were recorded using NaCl solution cells (CH_2Cl_2) on a Mattson Polaris Fourier transform IR spectrometer, FAB (positive ion) mass spectra using an AutoSpec-Q mass spectrometer, 35 keV Cs^+ primary ion beam and 3-nitrobenzyl alcohol as matrix ($eV \approx 1.60 \times 10^{-19} \text{ J}$). Microanalyses were carried out in the Department of Chemistry, Imperial College of Science, Technology and Medicine.

Electrochemistry

Anhydrous dichloromethane (packaged under nitrogen, 100 cm^3 bottles, Aldrich) for electrochemistry and tetrabutylammonium hexafluorophosphate supporting electrolyte (dried and stored in a vacuum oven at 40°C , Fluka) were commercial products. The cyclic voltammetric measurements were performed with a BAS 100A electrochemical analyser.²³ A three-electrode cell was designed to allow the tip of the saturated calomel electrode (SCE) to approach closely, *via* a Luggin capillary, the platinum disc working electrode, which in turn was surrounded by a platinum spiral counter electrode. Controlled potential coulometry was carried out by using a AMEL model 552 potentiostat, connected to a model 558 integrator. A three-compartment cell was designed with a central unit bearing a platinum gauze working macroelectrode. The lateral compartments contained the reference (SCE) and the auxiliary (mercury pool) electrodes, respectively. The compartments containing the working and the auxiliary electrodes were separated by a sintered-glass disc. *In situ* visible spectra of products electrogenerated by macroelectrolysis were recorded with a Lambda 2 Fibre Optic System UV/VIS spectrometer (Perkin-Elmer). Deoxygenation of the solutions was achieved by bubbling ultrapure nitrogen for at least 10 min. All the potential values are referred to the SCE and under the present experimental conditions the one-electron oxidation of ferrocene occurs at $+0.35 \text{ V}$, displaying a peak-to-peak separation of 82 mV at 0.2 V s^{-1} .

Synthesis

The complexes *cis*- $[\text{RuCl}_2(\text{dppm})_2]$, *cis*- $[\text{OsCl}_2(\text{dppm})_2]$ and $[\text{RuCl}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]$ were prepared by literature methods,²⁴

as was 1,3,5-triethynylbenzene²⁵ and ferrocenium hexafluorophosphate.²⁶ The complexes **1–7** were formed from the aforementioned species using the following general methods adapted from literature procedures.^{3p,10j}

Representative reaction to synthesize complexes 1–4. The ratio of the reagents and metal used varies, along with the reaction times, see Results and Discussion section. Freshly sublimed 1,3,5-triethynylbenzene (17.9 mg, 0.12 mmol) and *cis*-[RuCl₂(dppm)₂] (112 mg, 0.12 mmol) were dissolved in CH₂Cl₂ (15 cm³). Sodium hexafluorophosphate (20 mg, 0.24 mmol) was then added and the mixture stirred for 4 h, during which time a yellow to red-orange change was observed. The solution was filtered to remove any excess of NaPF₆ and NaCl by-product and dbu (2 drops) was added to the vinylidene solution and stirring continued for 2 h. The resulting yellow solution was filtered and the solvent removed *in vacuo*. The residue was redissolved in CH₂Cl₂–hexane and following slow solvent evaporation complex **1** was isolated as a fine yellow powder which was washed with cold hexane. This powder could be further purified by reprecipitation from a CH₂Cl₂–hexane two-layered system. Yield 78.8 mg (63%) (Found: C, 68.4; H, 4.5. C₆₂H₄₉ClP₄Ru·CH₂Cl₂ requires C, 66.4; H, 4.5%); $\tilde{\nu}/\text{cm}^{-1}$ (CH₂Cl₂) 2071 (C≡C) and 3300 (C≡C–H); $\delta_{\text{H}}(\text{CDCl}_3)$ 8.0–7.0 (40 H, m, C₆H₅, C₆H₃), 4.93 (4 H, m, PCH₂P) and 3.07 (2 H, s, C≡CH); $\delta_{\text{P}}(\text{CDCl}_3)$ –5.9; *m/z* 1054 (*M*⁺), 1019, 905 and 869.

trans-[HC≡CC₆H₃{C≡CRu(dppm)₂Cl}₂] **2**. Yield 20 mg (20%) (Found: C, 66.8; H, 4.3. C₁₁₂H₉₂Cl₂P₈Ru₂·CH₂Cl₂ requires C, 66.4; H, 4.7%); $\tilde{\nu}/\text{cm}^{-1}$ (CH₂Cl₂) 2068 (C≡C) and 3304 (C≡C–H); $\delta_{\text{H}}(\text{CDCl}_3)$ 8.0–7.0 (80 H, m, C₆H₅, C₆H₃), 4.93 (8 H, m, PCH₂P) and 2.94 (1 H, s, C≡CH); $\delta_{\text{P}}(\text{CDCl}_3)$ –5.7; *m/z* 1959 (*M*⁺), 1054, 905 and 869.

trans-[(HC≡C)₂C₆H₃C≡COs(dppm)₂Cl] **3**. Yield 93.0 mg (50%) (Found: C, 62.2; H, 3.9. C₆₂H₄₉ClO₂P₄·CH₂Cl₂ requires C, 61.6; H, 4.2%); $\tilde{\nu}/\text{cm}^{-1}$ (CH₂Cl₂) 2066 (C≡C) and 3302 (C≡C–H); $\delta_{\text{H}}(\text{CDCl}_3)$ 8.0–7.0 (40 H, m, C₆H₅, C₆H₃), 4.92 (4 H, m, PCH₂P) and 3.05 (2 H, s, C≡CH); $\delta_{\text{P}}(\text{CDCl}_3)$ –48.4; *m/z* 1145 (*M*⁺), 995, 959, 759, 573, 495, 417 and 375.

trans-[HC≡CC₆H₃{C≡COs(dppm)₂Cl}₂] **4**. Yield 53.0 mg (30%) (Found: C, 61.1; H, 4.3. C₁₁₂H₉₂Cl₂Os₂P₈·CH₂Cl₂ requires C, 61.3; H, 4.2%); $\tilde{\nu}/\text{cm}^{-1}$ (CH₂Cl₂) 2064 (C≡C) and 3304 (C≡C–H); $\delta_{\text{H}}(\text{CDCl}_3)$ 8.0–7.0 (80 H, m, C₆H₅, C₆H₃), 4.90 (8 H, m, PCH₂P) and 3.02 (1 H, s, C≡CH); $\delta_{\text{P}}(\text{CDCl}_3)$ –47.0; *m/z* 2138 (*M*⁺), 2102, 1145, 1070 and 1023.

Complexes 5–7. These were prepared using two methods adapted from literature procedures.^{3p,10a} The first was similar to that described for complexes **1–4** but resulted in low yields of products (**5**, **20**; **6**, **17%**) so the second method was preferred for **5–7**.

The complex [RuCl(η-C₅H₅)(PPh₃)₂] (121 mg, 0.17 mmol) was heated to reflux in methanol (20 cm³) for 15–20 min to give an orange-red suspension to which 1,3,5-triethynylbenzene (25 mg, 0.17 mmol) was then added. The mixture was stirred and heated to reflux for 20 min and then cooled to room temperature. Addition of 2–3 equivalents of sodium resulted in rapid precipitation of a yellow powder. The mixture was stirred for 1 h, filtered and the yellow solid washed with cold methanol. The product could be further purified by reprecipitation from a CH₂Cl₂–hexane two-layered system (84 mg, 60%) (Found: C, 70.2; H, 4.8. C₅₃H₄₀P₂Ru·CH₂Cl₂ requires C, 70.1; H, 4.6%); $\tilde{\nu}/\text{cm}^{-1}$ (CH₂Cl₂) 2063 (C≡C) and 3301 (C≡C–H); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.7–6.9 (33 H, m, C₆H₅, C₆H₃), 4.36 (5 H, s, C₅H₅), 3.01 (1 H, s, C≡C–H) and 2.97 (1 H, s, C≡C–H); $\delta_{\text{P}}(\text{CDCl}_3)$ 50.9; *m/z* 840 (*M*⁺), 691, 579, 501, 429 and 350.

[HC≡CC₆H₃{C≡CRu(η-C₅H₅)(PPh₃)₂}₂] **6**. Yield 182 mg (60%) (Found: C, 70.9; H, 4.7. C₉₃H₇₄P₄Ru₂·CH₂Cl₂ requires C, 70.7; H, 4.7%); $\tilde{\nu}/\text{cm}^{-1}$ (CH₂Cl₂) 2064 (C≡C) and 3302 (C≡C–H); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.7–6.9 (63 H, m, C₆H₅, C₆H₃), 4.34 (10

H, s, C₅H₅) and 3.01 (1 H, s, C≡C–H); $\delta_{\text{P}}(\text{CDCl}_3)$ 51.0; *m/z* 1530 (*M*⁺) and 1267.

[C₆H₃{C≡CRu(η-C₅H₅)(PPh₃)₂}₃] **7**. Yield 243 mg (66%) (Found: C, 71.0; H, 5.0. C₁₃₅H₁₀₈P₆Ru₃·CH₂Cl₂ requires C, 70.8; H, 4.8%); $\tilde{\nu}/\text{cm}^{-1}$ (CH₂Cl₂) 2065 (C≡C); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.7–6.9 (93 H, m, C₆H₅, C₆H₃) and 4.34 (15 H, s, C₅H₅); $\delta_{\text{P}}(\text{CDCl}_3)$ 51.3; *m/z* 2219 (*M*⁺), 1958, 1696, 1530 and 1171.

Complexes 8–10. These were prepared by following a literature procedure¹⁶ and the formation of complex **10** is detailed as a representative example. The complex [C₆H₃{C≡CRu(η-C₅H₅)(PPh₃)₂}₃] (40 mg, 0.018 mmol) was dissolved in dry CH₂Cl₂ (10 cm³) and the solution cooled to –78 °C. Ferrocenium hexafluorophosphate (10 mg, 0.036 mmol) was then added and on warming to room temperature a colour change was noted. The mixture was stirred at room temperature for 2 h and then reduced to dryness *in vacuo*. After washing with hexane (2 × 10 cm³) the product was isolated as a dark brown microcrystalline solid (27 mg, 60%). $\tilde{\nu}/\text{cm}^{-1}$ (Nujol) 2059 (C≡C, non-oxidised site) and 1978 (=C=C=, oxidised site); $\delta_{\text{P}}(\text{CDCl}_3)$ 51.6, 42.5 (spt) and –143.6.

[HC≡CC₆H₃{C≡CRu(η-C₅H₅)(PPh₃)₂}₂][PF₆] **8**. Yield 15 mg (60%); $\tilde{\nu}/\text{cm}^{-1}$ (Nujol) 2060 (C≡C, non-oxidised site) and 1973 (=C=C=, oxidised site); $\delta_{\text{P}}(\text{CDCl}_3)$ 51.0, 42.3 (spt) and –143.6.

[C₆H₃{C≡CRu(η-C₅H₅)(PPh₃)₂}₂][PF₆] **9**. Yield 18 mg (64%); $\tilde{\nu}/\text{cm}^{-1}$ (Nujol) 2060 (C≡C, non-oxidised site) and 1972 (=C=C=, oxidised site); $\delta_{\text{P}}(\text{CDCl}_3)$ 51.3, 42.5 (spt) and –143.6.

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