Syntheses and molecular structures of *trans*-bis(alkynyl) *tetrakis*-triethylphosphite ruthenium complexes.

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Dedicated to Professor John A. Gladysz on the occasion of his 65th birthday and in
celebration of a career of academic achievement.

Abstract

A simple synthesis of complexes *trans*-[Ru(C≡CC₆H₄-4-R)₂{P(OEt)₃}₄] from *trans*-[RuCl₂{P(OEt)₃}₄] and the terminal alkyne is described. Crystallographically determined molecular structures indicate a range of conformers, with the ethynyl arylene rings differing in their orientation with respect to each other across the Ru{P(OEt)₃}₄ fragment. Electrochemical analysis reveals a well-behaved one-electron oxidation process, which is only some 100 mV more positive than the analogous *trans*-[Ru(C≡CC₆H₄-4-R)₂(dppe)₂] complexes. Quantum chemical calculations reveal largely delocalised electronic structures and suggest that these compounds may find use as wire-like molecules within single molecule electronics.

1. Introduction

The chemistry of *trans*-bis(alkynyl) complexes of ruthenium has been extensively developed over the past decades, and whilst the vast majority are supported by ancillary phosphine ligands,[1-4] examples with other supporting ligand sets, including, for example, mixed phosphine-carbonyl[5,6] or N-heterocyclic carbene-carbonyl[7] ligand sets, macrocyclic amines and dioxodiazamacrocycles [8,9] are also known. In addition to finding extensive application as building blocks and donors for the construction of NLO active materials,[10,11] including chemically and redox-switchable examples,[12,13] donor molecules within solar cells[14-16] and applications as sensors,[17] *trans*-[Ru(C≡CR)₂(dppe)₂] [dppe = 1,2-bis(diphenylphosphino)ethane] complexes systems commonly feature in designs of metal-containing molecular wires.[18,19] The development of mechanically controlled break-junctions and molecular junctions based on the use of a scanning tunnelling microscope (STM) tip to contact a single molecule now allows the investigation of molecular compounds and complexes at the molecular level as active components in prototypical electronic devices.[20,21] In one of the earliest examples of these investigations, the single-molecule conductance of the organometallic complex, *trans*-[Ru(C≡CC₆H₄-4-SAc)₂(dppm)₂] was compared with that of the organic compound, AcSC₆H₄-4-C≡CC₆H₄-4-C≡CC₆H₄-4-SAc in Au|molecule|Au junctions via the STM break junction.[22] The organometallic complex exhibited a higher single molecular conductance value ($2.45 \pm 0.90 \times 10^{-4} G_0$ vs. $0.46 \pm 0.26 \times 10^{-4} G_0$), although the β decay constants calculated using the STM apparent height method[23] of the two wires are comparable ($1.01 \pm 0.25 \text{ \AA}^{-1}$ vs. $1.11 \pm 0.18 \text{ \AA}^{-1}$). More recently, it was shown that conductance histograms generated from *trans*-[Ru(C≡CC₆H₄-4-C≡CSiMe₃)₂(dppe)₂] and Me₃SiC≡CC₆H₄-4-C≡CC₆H₄-4-C≡CC₆H₄-

4-C≡CSiMe₃, by the *I(s)* method[24] were simplified in comparison with the thiolate-contacted compounds, with trimethylsilylethynyl binding groups giving only a single, narrow conductance peak as the steric bulk of the termini restricts the range of available, conductive contacts.[25] A higher conductance value was again obtained for the organometallic complex ($5.10 \pm 0.99 \cdot 10^{-5} G_0$) compared with the organic analogue.[26] Efforts are now being expended on the preparation and measurement of longer, multi-metallic organometallic wires of ruthenium[27-29] and other metals[30-32] which have clearly demonstrated the potential for organometallic compounds of this *trans*-bis(alkynyl) type to find application in molecular electronic platforms. Excitingly, the results of many years effort are now beginning to show promise within genuine electronic devices. [21,33,34]

In seeking to optimise the performance of metal complex molecular wires based on *trans*-M(C≡CR)₂L_n frameworks, attention has been drawn to the role that the ancillary ligands L might play on tuning alignment of the critical molecular orbitals with the electrode Fermi levels.[35] Recently, both the Akita group[36] and our own[37] have been attracted to the potential that trialkylphosphite ligands might play as ancillary groups in such structures. The majority of synthetic routes to *trans*-bis(alkynyl) complexes bearing *tetrakis*-trialkylphosphite fragments, *trans*-[Ru(C≡CR)₂{P(OR)₃}₄] (where X = Me, Et) involve treatment of *trans*-[RuCl₂{P(OR)₃}₄] with alkynyl-lithium reagents and afford the bis(alkynyl) products in *ca.* 35-45 % yield.[36,38] Compounds prepared in this manner include *trans*-[Ru(C≡CR)₂{P(OEt)₃}₄] (R = Ph ([**1a**]), [38] C₆H₄-4-Me, [38] ^tBu, [38]) and *trans*-[Ru(C≡CC₅H₄N-4)₂{P(OMe)₃}₄].[36] Despite being air-stable and obtained in high isomeric purity, the bis(alkynyl) complexes are sensitive to reactions with electrophiles, forming alkynyl-vinylidene complexes, which may then undergo further rearrangement to form η³-butenyne complexes,[38,39] necessitating care on protic work-up.

We have recently observed that the complex *trans*-[Ru(C≡C-*cyclo*-3-C₄H₃S)₂{P(OEt)₃}₄] can be readily obtained from the slow reaction of *trans*-[RuCl₂{P(OEt)₃}₄] with 3-ethynyl thiophene, KPF₆ and NHⁱPr₂ in ethanol at room temperature.[37] Here we give further experimental details of this facile synthetic

route to complexes *trans*-[Ru(C≡CR)₂{P(OEt)₃}₄] that allows the complexes to be obtained in moderate to good yield. The crystallographically determined structures of seven new examples of this class of complex and electrochemical properties are described. Quantum chemical calculations reveal rather extensively delocalised frontier orbitals in these wire-like molecules.

2. Results and Discussion

2.1 Syntheses

The key starting material for these studies, *trans*-[RuCl₂{P(OEt)₃}₄], is readily obtained from RuCl₃.nH₂O and P(OEt)₃ upon treatment with NaBH₄. [40] Reaction of *trans*-[RuCl₂{P(OEt)₃}₄] with KPF₆ (4 equivalents) and an excess of a terminal alkyne, HC≡CR, in a mixed EtOH/NHⁱPr₂ solvent resulted in the slow formation of complexes *trans*-[Ru(C≡CR)₂{P(OEt)₃}₄] (Scheme 1). Although conversions took days to weeks to completion, the resulting products were readily isolated from the reactions mixtures by precipitation and crystallisation and obtained in moderate to good yields (34 – 85 %), with the exception of the ethynylbenzonitrile complex [**1e**]. The yield of [**1e**] (19 %) was considerably lower due to the formation of additional side products during the reaction and presumably a consequence of competing coordination reactions of the nitrile group and formation of oligomers of poorly defined composition. Similar complication are also known in analogous chemistry of *trans*-Ru(dppe)₂-based complexes. [41] Monitoring of the reactions by *in situ* ³¹P{¹H} NMR spectroscopy suggests that the formation of [**1**] proceeds via an intermediate *mono*-alkynyl complex, *trans*-[RuCl(C≡CR){P(OEt)₃}₄], with resonances from an intermediate complex comparable with the *mono*-alkynyl *tetrakis*-triethylphosphite complex *trans*-[RuCl(C≡CC₆H₅){P(OEt)₃}₄] (³¹P{¹H} NMR (CD₂Cl₂): δ 132.3 ppm), [42] being observed (Figure S1).

Scheme 1. The preparation of complexes **[1a-h]**

Evidence for the formation of **[1a-h]** includes triplet and quartet resonances in the ^1H NMR spectra corresponding to the $-\text{CH}_3$ and $-\text{CH}_2-$ ethyl fragments (respectively) on the four equivalent phosphite groups about the ruthenium centre. Resonances occur between δ 1.18 – 1.21 ppm (CH_3) and δ 4.25 – 4.32 ppm (CH_2) with mutual $^3J_{\text{HH}}$ couplings of 7 Hz. Singlet resonances in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, between δ 136.2 – 139.5 ppm, support the *trans*-arrangement of the alkynyl ligands. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, quintet (or unresolved multiplet) resonances between δ 89.9 – 131.6 ppm for the Ru-C α -carbons coupled to the four *cis*-phosphorus nuclei ($^2J_{\text{CP}} = 19 - 21$ Hz), and singlet resonances between δ 104.9 – 116.9 ppm for the Ru-C $\equiv$ C β -carbons confirmed the presence of the alkynyl ligand. In the IR spectra, $\nu(\text{RuC}\equiv\text{C})$ bands observed between 2055 – 2147 cm^{-1} further support alkynyl functionality. Finally, the structures **[1b-h]** have been determined by single crystal X-ray diffraction studies (see section 5.3.2), which confirmed the structural assignments based on spectroscopy.

The use of alternative halide-abstracting agents in the formation of [**1b**], by way of example, was also briefly examined. The analogous reaction sequence to that shown in Scheme 1 but with NaPF₆ rather than KPF₆ gave [**1b**] in lower yield (56 %) after a 13 day reaction (c.f. 86% isolated yield from the reaction in Scheme 1). With TlBF₄ as the halide abstracting agent, the reaction sequence is again similar, with slow generation of [**1b**] via the *mono*-alkynyl intermediate. However, in this case, the conversion from the intermediate *mono*-alkynyl complex to the product *trans*-bis(alkynyl) was not complete, even after the addition of excess TlBF₄ and alkyne and a reaction length of 14 days. Given the extreme toxicity of Tl(I) salts, and subsequent increased difficulty of work-up procedures, this route is not considered optimal. With AgOTf, a plethora of unassigned resonances were observed in the *in situ* ³¹P NMR spectrum, evincing a complex mixture of products in solution. The propensity of Ag(I) salts to coordinate to other species in the reaction mixture (such as chlorides and alkynes) has been previously demonstrated,[43-45] and similar processes are likely associated with the range of compounds observed here.

2.2 Molecular Structures

Single crystal X-ray structure determinations have been made for *trans*-[Ru(C≡CPh)₂{P(OEt)₃}₄] ([**1b**]), *trans*-[Ru(C≡CC₆H₄-4-C≡CSiMe₃)₂{P(OEt)₃}₄] ([**1c**]) as a CHCl₃ solvate, *trans*-[Ru(C≡CC₆H₄-4-CO₂Me)₂{P(OEt)₃}₄] ([**1d**]) as a CH₂Cl₂ solvate, *trans*-[Ru(C≡CC₆H₄-4-C≡N)₂{P(OEt)₃}₄] ([**1e**]), *trans*-[Ru(C≡CC₆H₄-4-NO₂)₂{P(OEt)₃}₄] ([**1f**]), *trans*-[Ru(C≡CC₆H₄-4-C₅H₁₁)₂{P(OEt)₃}₄] ([**1g**]) and *trans*-[Ru(C≡CC₆H₄-4-OMe)₂{P(OEt)₃}₄] [**1h**], with important bond lengths and bond angles summarised in Table 1 and Table 2. The atom labelling

scheme is shown in Figure 1, and the definition of the angles θ^a and $\theta^{a'}$ shown in Figure 2. Plots of other molecules are given in the Supporting Information.

Figure 1. A plot of a molecule of **1h**, with hydrogen atoms and one component of a disordered ethyl group omitted for clarity, showing the atom labelling scheme. Ellipsoids are drawn at the 50 % probability level. Crystallographic data for the structure were collected at 100(2) K on an Oxford Diffraction Gemini diffractometer with Mo K α radiation. One ethyl group was modeled as being disordered over two sets of sites with occupancy factors constrained to 0.5 after trial refinement. Geometries and displacement parameters of the disordered components were restrained to reasonable values.

Figure 2. Representation of angles θ^a and $\theta^{a'}$ in *trans*-[Ru(C≡CR)₂{P(OEt)₃}₄] complexes ([**1b-h**]), as being the smallest C_{ortho}-C_{ipso}-Ru-P(any) torsion angles (irrespective of sign) calculated for each of the two aryl rings (depicted as red and blue lines) on the *trans*-bis(aryl) alkynyl fragments.

Table 1: Selected bond distances (Å), C_{ortho}-C_{ipso}-Ru-P(any) torsion angles (θ^a , $\theta^{a'}$ / °) and angles between planes containing the aryl-ring fragments (θ^p / °) for *trans*-[Ru(C≡CR)₂{P(OEt)₃}₄] complexes [**1b** – **h**].

Complex	R	Ru-C ¹	Ru-C ³	C ¹ ≡C ²	C ³ ≡C ⁴	Ru-P	Ru-P _{avg}	θ^a , $\theta^{a'}$	θ^p
[1b] ^a	C ₆ H ₅	2.066(3)	-	1.207(4)	-	2.3166(9), 2.3245(9)	2.323	− 12.2, 40.8	61.2
[1c]	C ₆ H ₄ -4-C≡CSiMe ₃	2.056(3)	2.062(4)	1.218(5)	1.214(5)	2.327(1), 2.328(1), 2.316(1), 2.309(1)	2.320	23.8, 42.0	22.2
[1d]	C ₆ H ₄ -4-CO ₂ Me	2.050(5)	-	1.217(7)	-	2.292(3), 2.300(3), 2.322(3), 2.331(3)	2.311	16.3, − 22.6	83.6
[1e]	C ₆ H ₄ -4-C≡N	2.053(3)	2.052(3)	1.213(4)	1.213(4)	2.3155(7), 2.3156(7), 2.3161(7), 2.3170(7)	2.316	9.4, − 27.2	79.7
[1f]	C ₆ H ₄ -4-NO ₂	2.059(2)	2.063(2)	1.214(3)	1.214(3)	2.3161(6), 2.3167(6), 2.3176(6), 2.3199(6)	2.318	− 39.1, 22.9	26.0
[1g]	C ₆ H ₄ -4-C ₅ H ₁₁	2.072(2)	2.075(2)	1.210(3)	1.218(3)	2.3129(6), 2.3133(6), 2.3175(6), 2.3178(5)	2.315	16.4, 22.6	69.7
[1h]	C ₆ H ₄ -4-OMe	2.078(2)	2.066(2)	1.207(3)	1.204(3)	2.3041(6), 2.3061(6), 2.3123(6), 2.3138(6)	2.309	29.3, − 18.2	13.9
<i>planar</i> -[1h']	<i>C₆H₄-4-OMe</i>	<i>2.089</i>	<i>2.089</i>	<i>1.223</i>	<i>1.223</i>	<i>2.351, 2.352,</i> <i>2.354, 2.355,</i>	<i>2.353</i>	<i>21.9, -18.6</i>	<i>3.9</i>
<i>perp</i> -[1h']	<i>C₆H₄-4-OMe</i>	<i>2.089</i>	<i>2.089</i>	<i>1.223</i>	<i>1.223</i>	<i>2.351, 2.352,</i> <i>2.353, 2.353</i>	<i>2.352</i>	<i>23.3, -23.1</i>	<i>-89.9</i>

^a From one component of the disorder model.

Table 2: Selected bond angles (°) for *trans*-[Ru(C≡CR)₂{P(OEt)₃}₄], [**1b** – **h**].

Complex	R	C ³ -Ru-C ¹	Ru-C ¹ -C ²	Ru-C ³ -C ⁴	P-Ru-P (<i>cis</i>)	P-Ru-P (<i>trans</i>)
[1b]	C ₆ H ₅	180.0	180.0	180.0	90.27(4), 89.74(4)	179.93(6), 171.46(5)
[1c]	C ₆ H ₄ -4-C≡CSiMe ₃	178.8(1)	178.5(3)	179.6(3)	89.99(3), 91.56(4), 89.97(4), 89.23(4)	172.17(4), 174.39(4)
[1d]	C ₆ H ₄ -4-CO ₂ Me	179.8(4)	178.8(6)	179.8(4)	90.36(12), 89.69(10), 89.37(11), 92.17(11)	172.25(10), 167.90(10)
[1e]	C ₆ H ₄ -4-C≡N	179.5(1)	175.2(2)	178.6(2)	89.76 (3), 90.29(3), 89.80(3), 91.09(3)	173.03(3), 172.13(3)
[1f]	C ₆ H ₄ -4-NO ₂	178.7(1)	176.3(2)	178.7(2)	88.87(2), 89.89(2), 91.33(2), 90.70(2)	173.39(2), 172.87(2)
[1g]	C ₆ H ₄ -4-C ₅ H ₁₁	178.3(1)	177.7(2)	176.5(2)	89.31(2), 91.91(2), 90.68(2), 88.83(2)	174.43(2), 172.44(2)
[1h]	C ₆ H ₄ -4-OMe	177.7(2)	178.8(2)	175.7(2)	89.25(2), 89.34(2), 90.75(2), 92.44(2)	168.56(2), 170.81(2)
<i>planar</i> -[1h']	C ₆ H ₄ -4-OMe	179.7	179.3	179.22	89.97, 90.10, 90.27, 90.30	173.88, 174.07
<i>perp</i> -[1h']	C ₆ H ₄ -4-OMe	179.9	179.6	180.0	90.18, 90.18, 90.18, 90.20,	173.44, 173.43

Although the mixed alkynyl-vinylidene complex, *trans*-[Ru(C $\equiv$ CC₆H₅)(=C=CMeC₆H₅){P(OEt)₃}₄]OTf, has been structurally characterised,[38] the series of complexes [**1b** - **h**] represents the first structurally characterised *trans*-bis(alkynyl) derivatives of the type *trans*-[Ru(C $\equiv$ CR)₂{P(OR)₃}₄]. For all cases, [**1b** - **h**], the P-Ru-P bond angles between *cis*-phosphines (*ca.* 90 °) and those between *trans*-phosphines (*ca.* 180 °) in addition to $\equiv$ C-Ru-C $\equiv$ angles (*ca.* 180 °), indicate the octahedral geometry about the ruthenium centre, in agreement with the previously published alkynyl-vinylidene complex.[38]

Orpen and Connelly have summarised geometric variations in a series of metal-phosphine and phosphite complexes, and similar trends are observed here.[46] In general, the M-PX₃ (X = R, OR; R = alkyl, aryl) bond length increases upon oxidation of the metal centre, evincing M-PX₃ π -back-bonding. The P-X bonds are correspondingly shortened on oxidation, implicating P(σ^*), the predominantly anti-bonding combination of P(3*p*_{*x,y*}) with X(σ), as the acceptor orbital in the back-bonding model. The P(σ^*) orbital is lowered in energy when X is more electronegative and the PX₃ fragment is made more pyramidal as stabilising overlap between P(3*p*_{*x,y*}) and X(σ) decreases when the X atoms move out of the *xy* plane. As a result, the π -accepting character of P(OEt)₃ (Tolman cone angle 109 °)[47] is expected to be far superior than PPh₃ (Tolman cone angle 145 °) and other related ligands bearing aromatic fragments, such as dppe and dppm. Hence for the crystallographically determined complexes [**1b-h**], variations in Ru-P bond lengths are anticipated to reflect the degree of Ru-P π -back-bonding.

The angles θ^a and $\theta^{a'}$ (Figure 2, Table 1) provide a convenient proxy measure for the alignment of the aryl π -systems, Ar(π), with Ru(*d*) on geometric grounds. Given the difficulty in defining a unique value for θ , with two indistinguishable aryl rings and four indistinguishable phosphite groups, θ^a and $\theta^{a'}$ values reported here represent the smallest C_{ortho}-C_{ipso}-Ru-P(any) torsion angles (irrespective of sign) measured for each of the two ring fragments (Figure 2). Therefore, in this case, angles close to 0 ° represent the most effective M(*d*)-C $\equiv$ C-Ar(π) overlaps and hence greatest correlation of structural and electronic properties.[48] As an indication of the extent of

delocalisation, θ^p values, representing the angle between planes containing the aryl ring fragments, are also given in Table 1. Angles with a higher deviation from 0° (perfectly ‘aligned’ ring systems) reflect more twisted conformations.

With the exception of [**1h**] ($\theta^p = 13.9^\circ$), and perhaps [**1c**] ($\theta^p = 22.2^\circ$) and [**1f**] ($\theta^p = 26.0^\circ$), the phenylene rings in these *bis*-aryl acetylide complexes [**1**] do not lie in the same plane (with θ^p values within the range $61.2 - 87.6^\circ$). In addition, complexes [**1**] generally display θ^a and $\theta^{a'}$ values between *ca.* $20 - 40^\circ$, and hence the $\text{Ar}(\pi)$ systems and $\text{Ru}(d)$ orbitals are not aligned for optimal overlap through the alkynyl π -system. In addition, whilst [**1e**] shows alignment of one $\text{Ar}(\pi)$ system with $\text{Ru}(d)$ ($\theta^a / \theta^{a'} = 9.4^\circ$), the second ring is not aligned, ($\theta^a / \theta^{a'} = -27.2^\circ$, $\theta^p = 79.7^\circ$). For these reasons, it is unsurprising to find that a definitive trend between Ru-P_{avg} and the electronic character of the aryl substituent does not exist. For example, the un-substituted complex [**1b**] has the longest Ru-P_{avg} bond length ($2.321 \text{ \AA}$) of the series. For all structures [**1b-h**], the $\text{Ru-C}(1, 3)$ bond lengths are consistent with single bond character, although complexes containing electron withdrawing *para*-substituents on the aromatic ring ([**1c**, **1d**, **1e**, **1f**]) are found to have generally shorter lengths ($2.050(5) - 2.059(2) \text{ \AA}$) than those bearing electron donating *para*-substituents ([**1g**, **h**] $2.072(2) - 2.078(2) \text{ \AA}$), evincing an electronic substituent effect, possibly propagated through the σ -framework. In this case, the un-substituted complex, [**1b**], has a $\text{Ru-C}(1)$ bond length between these two ranges ($2.066(3) \text{ \AA}$). For all cases, the $\text{C}\equiv\text{C}$ bond lengths are consistent with triple bond character. Differences in $\text{C}\equiv\text{C}$ bond lengths as a result of the R substituent are found to be within statistical error.

2.3 Electrochemistry

The electrochemical responses of *trans*-bis(alkynyl) *tetrakis*-triethylphosphite complexes [**1a-h**] in CH_2Cl_2 solutions containing 0.1 M $[\text{N}^n\text{Bu}_4]\text{PF}_6$ were examined by cyclic voltammetry (Table 3). Potentials are quoted against the ferrocene / ferrocenium couple ($[\text{Fe}\{\eta^5\text{-C}_5\text{H}_5\}_2] / [\text{Fe}\{\eta^5\text{-C}_5\text{H}_5\}_2]^+ = 0.00 \text{ V}$) using an internal decamethylferrocene / decamethylferrocenium reference ($[\text{Fe}\{\eta^5\text{-C}_5\text{Me}_5\}_2] / [\text{Fe}\{\eta^5\text{-C}_5\text{Me}_5\}_2]^+$).

$\text{C}_5\text{Me}_5\text{]}_2]^+ = -0.48 \text{ V})$. [49,50] These data represent the first electrochemical exploration of *trans*-bis(alkynyl) complexes containing the *trans*- $[\text{Ru}(\text{C}\equiv\text{CR})_2\{\text{P}(\text{OEt})_3\}_4]$ motif.

Electrochemical reversibility describes the experiment where the rate of electron transfer is mass transport limited, and characterised by $i_{\text{pa}} / i_{\text{pc}} \approx 1$, $\Delta E_p \approx 60 \text{ mV}$ and $i_p \propto \nu^{1/2}$ (where i_{pa} = anodic peak current; i_{pc} = cathodic peak current; $\Delta E_p = |E_{\text{pc}} - E_{\text{pa}}|$, ν = scan rate). The *trans*-bis(alkynyl) complexes [**1a-g**] exhibit two oxidation events. In addition, the nitro-phenyl complex [**1f**] exhibits a reduction wave, assigned to the closely occurring independent reductions of the two nitro groups on the basis of the higher peak current, and large ΔE_p value (220 mV) in comparison with the internal standard (60 mV). The complex [**1h**], which contains the most electron donating substituent, exhibits three oxidation events. There was evidence of electrochemical-chemical (EC) behavior in the first oxidation process of [**1a**] with $i_{\text{pa}} > i_{\text{pc}}$ at room temperature, and additional electrochemical processes indicative of new chemical species being observed on the reverse scan when conducting the experiment. At reduced temperatures (ca. -20°C), current ratios approached unity, indicating improvements to the chemical reversibility. The second oxidation processes (and third for [**1h**]) are irreversible at all temperatures.

Table 3. Selected electrochemical data (V) of [**1a-h**] from solutions in 0.1 M [NBu₄][PF₆] / CH₂Cl₂ at room temperature.

Complex	R	E _{1/2} (1)	E _{1/2} (2)	E _{1/2} (3)	E _{1/2} (red)	ΔE ₁₋₂	ΔE ₂₋₃
[1a]	C ₄ H ₉	− 0.09 ^b	0.83 ^c	-	-	0.92	-
[1b]	C ₆ H ₅	0.09 ^a	0.85 ^c	-	-	0.76	-
[1c]	C ₆ H ₄ -4- C≡CSiMe ₃	0.14 ^a	0.89 ^c	-	-	0.75	-
[1d]	C ₆ H ₄ -4- CO ₂ Me	0.19 ^a	0.88 ^c	-	-	0.69	-
[1e]	C ₆ H ₄ -4-CN	0.30 ^a	0.83 ^c	-	-	0.53	-
[1f]	C ₆ H ₄ -4-NO ₂	0.38 ^a	0.93 ^c	-	− 1.73 ^d	0.55	-
[1g]	C ₆ H ₄ -4- C ₅ H ₁₁	0.02 ^a	0.74 ^c	-	-	0.72	-
[1h]	C ₆ H ₄ -4-OMe	− 0.11 ^a	0.39 ^c	0.81 ^c	-	0.50	0.42

^areversible; ^breversibility improves at lower temperatures (−20°C) ; ^cirreversible;

^dtwo-electron redox event

The electronic effects of the R group on molecular properties are expected to be more apparent in the solution state over the solid state, as a result of greater conformational freedom, which permits better overlap and conjugation through the molecular backbone. The first oxidation potentials (E_{1/2}(1)) span a 500 mV range (Table 3), and display a clear dependence on the electronic characteristics of the aryl substituent. As with other ruthenium alkynyl complexes,[51] the oxidation processes are presumably largely centered on the alkynyl ligand(s). Similar trends in redox potentials are also displayed in *trans*-bis(alkynyl) complexes containing the {Ru(dppe)₂} motif.[48]

These $\{\text{Ru}\{\text{P}(\text{OEt})_3\}_4\}$ containing complexes have higher (more positive) oxidation potentials (by *ca.* + 0.10 V), than the analogous $\{\text{Ru}(\text{dppe})_2\}$ complexes reflecting the increased π -accepting character of phosphite ligands.[46,48] In contrast, $E_{1/2}(2)$ is less sensitive to the nature of the R group, where values fall within a narrower 150 mV range. The additional anodic redox event observed for [**1h**] is thought to arise as a result of the strongly electron donating alkynyl fragments and $\{\text{Ru}\{\text{P}(\text{OEt})_3\}_4\}$ although assignment to a ligand or metal based process is not obvious.

The plots of $E_{1/2}(1)$ vs Hammett parameter (σ_p)[52] are decidedly non-linear as is found for other parameters arising from organometallic metal acetylide complexes.[53,54] This likely arises from the decidedly mixed ($\text{M}(\text{d})-\text{C}\equiv\text{C}-\text{Ar}(\pi)$) electronic character of the metal alkynyl complexes and non-additive effects of *trans*-disposed ligands,[3,55] in addition to the effects of solvation and ion-pairing on electrode potentials that are not well captured by the Hammett parameters. Various attempts have been made arrive at more ‘electrochemically relevant’ parameters, most notably those by Lever [56] and Pickett. [57] However, these schemes assume metal-based oxidation and whilst excellent in the case of Werner-style coordination complexes and organometallic complexes with well-defined metal-based oxidation processes, [58] they are largely ill-suited to the ligand-based oxidation processes associated with complexes such as those described here. [48,59]

2.4 Quantum Chemical Calculations

To better understand the electronic structure of complexes *trans*-

$[\text{Ru}(\text{CCR})_2\{\text{P}(\text{OEt})_3\}_4]$ we turned to quantum chemical calculations of a simplified model of [**1h**], in which the ethyl groups of the phosphite ligands were replaced by

methyl groups. The simplified computational model complex, *trans*-[Ru(C≡CC₆H₄-4-OMe)₂{P(OMe)₃}₄] is denoted [**1h'**] for clarity. Geometry optimisation (CAM-B3LYP/LAN2DZ (Ru), 6-31G** all other atoms/COSMO(CH₂Cl₂) solvent model) was undertaken with two close lying minima being identified. One of these minima, denoted *planar*-[**1h'**] is remarkably similar to the crystallographically determined structure (Table 1), with the anisole rings being close to co-planar ($\theta^p = 3.9^\circ$) and almost aligned with a Ru-P bond ($\theta^a, \theta^{a'} = 21.9, -18.6^\circ$). A second minimum, only some 0.99 kJ/mol lower in energy features anisole rings that are essentially orthogonal ($\theta^p = 89.9^\circ$) and hence denoted *perp*-[**1h'**]. Geometries similar to *perp*-[**1h'**] are found in the crystallographic structures of [**1d**] and [**1e**] and it is very likely that the structures adopted in the crystal state owe more to crystal packing than any significant electronic effect.

Plots of the HOMO and LUMO of each conformer are given in Figure 3, and the energy and composition (%) of key frontier orbitals are given in Table 4. For the lowest energy conformer, *perp*-[**1h'**] a degenerate pair of orbitals that mix the ethynyl ligand π and Ru(*d*) orbitals and are distributed over the molecular framework form the HOMO and HOMO-1. Thus, despite the orthogonal arrangement of the anisole rings, the cosine-like dependence of the overlap of the anisole π , ethynyl π and Ru(*d*) orbitals mediates the extended delocalisation. In the case of *planar*-[**1h'**], the HOMO is well removed from the other orbitals in the occupied manifold, but also delocalised across the molecular backbone. In each conformer the LUMO is comprised of the ethynyl anisole π^* system.

Figure 3. Plots of the HOMO and LUMO of *planar*-[**1h'**] (left) and *perp*-[**1h'**] (right) with surfaces shown at $0.02 \text{ (e/bohr}^3)^{1/2}$.

Table 4. The energy (e / eV) and composition (%) of selected molecular orbitals of *planar*-[**1h'**] and *perp*-[**1h'**]

	eV	Ru	C(1)C(2)	C ₆ H ₄ OMe-1 ^a	C(3)C(4)	C ₆ H ₄ OMe-2 ^b	POMe ₃
<i>planar</i> -[1h']							
LUMO+2	1.35	0	1	49	0	48	1
LUMO+1	1.29	1	3	50	4	40	2
LUMO	1.14	2	9	38	9	39	2
HOMO	-6.02	20	21	21	18	18	2
HOMO-1	-6.49	0	18	24	21	30	7
HOMO-2	-6.67	39	23	1	30	2	5
<i>perp</i> -[1h']							
LUMO+2	1.35	1	1	14	3	80	2
LUMO+1	1.23	2	12	67	3	15	2
LUMO	1.22	2	3	15	12	67	2
HOMO	-6.15	18	14	12	26	25	4
HOMO-1	-6.15	18	26	25	14	12	4
HOMO-2	-7.16	17	31	10	24	7	11

^a the anisole group bonded to C(2). ^b the anisole group bonded to C(4)

Given the significant contribution of the ethynyl aromatic ligands to the HOMO(s) of these conformers of [**1h'**] it is very likely that the one-electron oxidation products of complexes [**1**] can be better described in terms of oxidation of the organic ligands, rather than in terms of Ru(II/III) couples.

3. Conclusion

Complexes of the general form *trans*-[Ru(C≡CR)₂{P(OEt)₃}₄] are readily obtained from *trans*-[RuCl₂{P(OEt)₃}₄], the terminal alkyne HC≡CR and KPF₆ in moderate to good yield, albeit over long reaction times; work-up is simple and the complexes obtained in good purity, and are readily crystallised. The compounds [**1a – h**] undergo a well-behaved one-electron oxidation at potentials only some 100 mV more positive than the well-known *trans*-[Ru(C≡CR)₂(dppe)₂] analogues. Quantum chemical calculations indicate extended delocalisation of π -type orbitals across the molecular backbone, which when coupled with the ability to introduce a range of surface binding groups through the mild synthetic methods described here, makes these complexes attractive candidates for the further development of metal-containing molecular wires.

4. Experimental

4.1 General considerations

All reactions were carried out under a dry, high-purity, nitrogen environment using oven dried (119 °C) glassware and standard Schlenk techniques, although no special precautions were taken in order to exclude air or moisture during work-up. The reaction solvent EtOH was dried over dry magnesium turnings and iodine whilst NHⁱPr₂ was dried over KOH and CH₂Cl₂ was dried over CaH₂. All other solvents

were reagent grade and used without further purification. The compounds $\text{HC}\equiv\text{CC}_6\text{H}_4\text{-4-NO}_2$, [60] $\text{HC}\equiv\text{CC}_6\text{H}_4\text{-4-CN}$, $\text{HC}\equiv\text{CC}_6\text{H}_4\text{-4-CO}_2\text{Me}$, [60] $\text{HC}\equiv\text{CC}_6\text{H}_4\text{-4-C}\equiv\text{CSiMe}_3$, [26] TlBF_4 , [61] and *trans*- $[\text{RuCl}_2\{\text{P}(\text{OEt})_3\}_4]$ [40] were synthesized by literature methods. All other reagents were commercially available and used as received.

NMR spectra were recorded at 25 ° C on Varian Inova 300 (^1H , 300.2 MHz; ^{31}P , 121.5 MHz) or Bruker Avance 600 (^1H , 600.1 MHz; ^{13}C , 150.9 MHz; ^{31}P , 242.9 MHz) spectrometers. Chemical shifts were determined relative to internal residual solvent signals (^1H , $\delta = 7.26$ ppm; ^{13}C , $\delta = 77.2$ ppm) or external 85% H_3PO_4 (^{31}P , $\delta = 0.0$ ppm). [62,63] FT-IR spectra were measured on a Nicolet Avatar 6700 or an Agilent Technologies Cary 660 spectrophotometer from solutions in CH_2Cl_2 in a thin layer cell fitted with CaF_2 windows. ESI-MS and APCI-MS were recorded on a Waters LCT Premier XE mass spectrometer in positive ion mode from solutions in methanol. Elemental analyses were carried out at London Metropolitan University.

Cyclic voltammetry was carried out using a Versastat 3 potentiostat with a platinum disc working electrode, a platinum wire counter electrode, and a platinum wire pseudo-reference electrode, from solutions in CH_2Cl_2 containing 0.1 M $[\text{N}^n\text{Bu}_4]\text{PF}_6$ as the electrolyte. Potentials are reported *vs.* the ferrocene / ferrocenium couple ($[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2] / [\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]^+ = 0$ V) using a decamethylferrocene / decamethylferrocenium internal standard ($[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)_2] / [\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)_2]^+ = -0.48$ V).

4.2 Syntheses of $\{Ru\{P(OEt)_3\}_4\}$ complexes and characterisation data

4.2.1 Synthesis of *trans*- $[Ru(C\equiv CC_4H_9)_2\{P(OEt)_3\}_4]$, [**1a**]

A mixture of *trans*- $[RuCl_2\{P(OEt)_3\}_4]$ (0.21 g, 0.25 mmol), KPF_6 (0.25 g, 1.3 mmol) and $HC\equiv CC_4H_9$ (0.18 ml, 1.6 mmol) in EtOH (5 ml) and NH^iPr_2 (2.5 ml) was stirred under N_2 for 15 days (or until all *mono*-alkynyl was converted to the *bis*-alkynyl complex in solution, monitored by unlocked $^{31}P\{^1H\}$ NMR spectroscopy). The solution colour changed from yellow to orange / brown over the reaction period and a white solid precipitated. The reaction solvents were removed under high vacuum, yielding a brown oily residue. A minimum amount of MeOH (*ca.* 3 ml) was added to the residue and solution stirred until a white solid separated out (*ca.* 5 minutes). The solution was left in an ice bath for *ca.* 20 minutes, to complete precipitation, before filtering. The collected white solid was washed with minimum cold MeOH (3×8 ml) and vacuum dried (0.10 g, 45 %). IR (CH_2Cl_2 , cm^{-1}): 2098 $\nu(RuC\equiv C)$. 1H NMR ($CDCl_3$, 300 MHz) δ / ppm: 0.83 (t, $J = 7$ Hz, 6H, H^6), 1.19 (t, $J = 7$ Hz, 36H, CH_3 , $P(OEt)_3$), 1.26 (quin., $J = 7$ Hz, 4H, H^4), 1.36 (sex., $J = 7$ Hz, 4H, H^5), 2.10 (t, $J = 7$ Hz, 4H, H^3), 4.27 (quar., $J = 7$ Hz, 24H, CH_2 , $P(OEt)_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 300 MHz) δ / ppm: 139.5 (s, $Ru\{P(OEt)_3\}_4$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 600 MHz) δ / ppm: 14.2 (s, C^6), 16.5 (s, CH_3 , $P(OEt)_3$), 22.3 (s, C^5), 22.4 (s, C^3), 33.4 (s, C^4), 60.8 (s, CH_2 , $P(OEt)_3$), 89.9 (quin., $J = 20$ Hz, C^1), 109.3 (s, C^2). ESI(+)-MS (m/z):

929 $[\text{Ru}(\text{C}\equiv\text{CC}_4\text{H}_9)_2\{\text{P}(\text{OEt})_3\}_4 + \text{H}]^+$, 888 $[\text{Ru}(\text{C}\equiv\text{CC}_4\text{H}_9)\{\text{P}(\text{OEt})_3\}_4 + \text{MeCN}]^+$, 879 $[\text{Ru}(\text{C}\equiv\text{CC}_4\text{H}_9)\{\text{P}(\text{OEt})_3\}_4 + \text{MeOH}]^+$, 847 $[\text{Ru}(\text{C}\equiv\text{CC}_4\text{H}_9)\{\text{P}(\text{OEt})_3\}_4]^+$.

4.2.2 Synthesis of *trans*- $[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_5)_2\{\text{P}(\text{OEt})_3\}_4]$, **[1b]**

A mixture of *trans*- $[\text{RuCl}_2\{\text{P}(\text{OEt})_3\}_4]$ (0.15 g, 0.18 mmol), KPF_6 (0.13 g, 0.73 mmol) and $\text{HC}\equiv\text{CC}_6\text{H}_5$ (0.2 ml, excess) in EtOH (5 ml) and NH^iPr_2 (2 ml) was stirred under N_2 for 11 days (or until all *mono*-alkynyl converted to the *bis*-alkynyl complex in solution, monitored by unlocked $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy). The solution colour changed from yellow to orange over the reaction period and a white solid precipitated. The reaction solvents were removed under high vacuum, yielding an orange / brown residue. The residue was extracted with minimum CH_2Cl_2 , filtered through Celite to remove reaction salts and concentrated to dryness by rotary evaporation, yielding an orange / brown residue. A minimum amount of MeOH (3 ml) was added to the residue and solution left in the fridge for *ca.* two hours to aid precipitation of a white solid. The solid was collected by filtration, washed with cold MeOH (3×10 ml) and air-dried (0.15 g, 85 %). The precipitate may be further purified by recrystallisation from CH_2Cl_2 / MeOH layer diffusion, yielding large white crystals suitable for X-ray crystallography. IR (CH_2Cl_2 , cm^{-1}): 2076 $\nu(\text{RuC}\equiv\text{C})$. ^1H NMR (CDCl_3 , 600 MHz) δ / ppm: 1.21 (t, $J = 7$ Hz, 36H, CH_3 , $\text{P}(\text{OEt})_3$), 4.31 (quar., $J = 7$ Hz, 24H, CH_2 , $\text{P}(\text{OEt})_3$), 6.94 (t, $J = 7$ Hz, 2H, H^6), 7.03 (d, $J = 8$ Hz, 4H, H^4), 7.11 (t, $J = 7$ Hz, 4H, H^5). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 300 MHz) δ / ppm: 138.2 (s, $\text{Ru}\{\text{P}(\text{OEt})_3\}_4$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 600 MHz) δ / ppm: 16.6 (s, CH_3 , $\text{P}(\text{OEt})_3$), 61.0 (s, CH_2 , $\text{P}(\text{OEt})_3$), 113.8 (s, C^2), 116.7 (quin., $J = 20$ Hz, C^1), 122.5 (s, C^6), 130.1 (s, C^4), 131.5 (s, C^3).

ESI(+)-MS (m/z): 969 $[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_5)_2\{\text{P}(\text{OEt})_3\}_4]^+$, 868 $[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_5)\{\text{P}(\text{OEt})_3\}_4]^+$.

Anal. Found: C, 49.37; H, 7.16. Calc for $\text{C}_{40}\text{H}_{70}\text{O}_{12}\text{P}_4\text{Ru}$: C, 49.57; H, 7.29 %.

4.2.3 Synthesis of *trans*- $[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-C}\equiv\text{CSiMe}_3)_2\{\text{P}(\text{OEt})_3\}_4]$, [**1c**]

A mixture of *trans*- $[\text{RuCl}_2\{\text{P}(\text{OEt})_3\}_4]$ (0.12 g, 0.15 mmol), KPF_6 (0.12 g, 0.65 mmol) and $\text{HC}\equiv\text{CC}_6\text{H}_4\text{-4-C}\equiv\text{CSiMe}_3$ (0.089 g, 0.45 mmol) in EtOH (4 ml) and NH^iPr_2 (1.5 ml) was stirred under N_2 for 17 days (or until all *mono*-alkynyl converted to the *bis*-alkynyl complex in solution, monitored by unlocked $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy). The solution colour changed from yellow to orange over the reaction period and a white solid precipitated. The reaction solvents were removed under high vacuum, yielding a brown oily residue. The residue was extracted with minimum CH_2Cl_2 , filtered through Celite to removed reaction salts and concentrated to dryness by rotary evaporation, yielding a brown oily residue. The residue was re-extracted with hexanes and filtered until extracts ran clear. The hexanes extracts were concentrated to dryness, yielding an orange solid. The orange solid was extracted a final time with minimum CH_2Cl_2 and filtered through a small alumina plug (basic, oven-dried). The first orange / yellow fraction was collected, concentrated to dryness yielding an orange solid, washed with minimum cold MeOH (3×3 ml) and air-dried (0.072 g, 43 %). Crystals suitable for single crystal X-ray crystallography were grown from a CHCl_3 / MeOH layer diffusion at reduced temperature (-18°C). IR (CH_2Cl_2 , cm^{-1}): 2147 $\nu(\text{C}\equiv\text{CSiMe}_3)$, 2068 $\nu(\text{RuC}\equiv\text{C})$. ^1H NMR (CDCl_3 , 600 MHz) δ / ppm: 0.22 (s, 18H, SiMe_3), 1.18 (t, $J = 7$ Hz, 36H, CH_3 , $\text{P}(\text{OEt})_3$), 4.27 (quar., $J = 7$ Hz, 24H, CH_2 ,

P(OEt)₃, 6.91 (d, $J = 8$ Hz, 4H, H⁴), 7.21 (d, $J = 8$ Hz, 4H, H⁵). ³¹P{¹H} NMR (CDCl₃, 300 MHz) δ / ppm: 137.6 (s, Ru{P(OEt)₃}₄). ¹³C{¹H} NMR (CDCl₃, 600 MHz) δ / ppm: 0.3 (s, SiMe₃), 16.6 (s, CH₃, P(OEt)₃), 61.0 (s, CH₂, P(OEt)₃), 93.5 (s, C⁸), 106.5 (s, C⁷), 114.8 (s, C³), 116.4 (s, C²), 123.3 (quin., $J = 20$ Hz, C¹), 129.8 (s, C⁴), 131.7 (s, C⁵). APCI(+)-MS (m/z): 1161 [Ru(C $\equiv$ CC₆H₄-4-C $\equiv$ CSiMe₃)₂{P(OEt)₃}₄ + H]⁺, 963 [Ru(C $\equiv$ CC₆H₄-4-C $\equiv$ CSiMe₃){P(OEt)₃}₄]⁺. Anal. Found: C, 51.90; H, 7.46. Calc. for C₅₀H₈₆O₁₂P₄RuSi₂: C, 51.71; H, 7.47.

4.2.4 Synthesis of *trans*-[Ru(C $\equiv$ CC₆H₄-4-CO₂Me)₂{P(OEt)₃}₄], [**1d**]

A mixture of *trans*-[RuCl₂{P(OEt)₃}₄] (0.17 g, 0.20 mmol), KPF₆ (0.23 g, 1.2 mmol) and HC $\equiv$ CC₆H₄-4-COOMe (0.21 g, 1.3 mmol) in EtOH (5 ml) and NHⁱPr₂ (2 ml) was stirred under N₂ for 20 days (or until all *mono*-alkynyl was converted to the *bis*-alkynyl complex in solution, monitored by unlocked ³¹P{¹H} NMR spectroscopy). The solution colour changed from yellow to orange / brown over the reaction period and a white solid precipitated. The reaction solvents were removed under high vacuum, yielding a brown oily residue. The residue was extracted with minimum CH₂Cl₂, filtered through Celite to remove reaction salts and concentrated to dryness by rotary evaporation, yielding an orange / brown oily residue. A minimum amount of MeOH (2.5 ml) was added to the residue and solution left in an ice bath to aid precipitation of a yellow solid (*ca.* 30 minutes). The solid was collected by filtration, washed with minimum cold MeOH (3 $\times$ 10 ml) and air-dried (0.12 g, 56 %). Large, yellow, needle-like crystals, suitable for X-ray crystallography, were grown from a

CH₂Cl₂ / MeOH layer diffusion. IR (CH₂Cl₂, cm⁻¹): 2066 ν(RuC≡C), 1706 ν(C=O), 1594 ν(C=C). ¹H NMR (CDCl₃, 300 MHz) δ / ppm: 1.19 (t, *J* = 7 Hz, 36H, CH₃, P(OEt)₃), 3.86 (s, 6H, OCH₃), 4.28 (quar., *J* = 7 Hz, 24H, CH₂, P(OEt)₃), 7.02 (d, *J* = 8 Hz, 4H, H⁴), 7.80 (d, *J* = 8 Hz, 4H, H⁵). ³¹P{¹H} NMR (CDCl₃, 300 MHz) δ / ppm: 137.3 (s, Ru{P(OEt)₃}₄). ¹³C{¹H} NMR (CDCl₃, 600 MHz) δ / ppm: 16.5 (s, CH₃, P(OEt)₃), 51.9 (s, OCH₃), 61.1 (s, CH₂, P(OEt)₃), 115.4 (s, C²), 123.7 (s, C³), 127.9 (quin., *J* = 20 Hz, C¹), 129.4 (s, C⁵), 130.0 (s, C⁴), 136.0 (s, C⁶), 167.7 (s, C=O). APCI(+)-MS (*m/z*): 1085 [Ru(C≡CC₆H₄-4-COOMe)₂{P(OEt)₃}₄ + H]⁺, 925 [Ru(C≡CC₆H₄-4-COOMe){P(OEt)₃}₄]⁺. Anal. Found: C, 48.64; H, 6.86. Calc. for C₄₄H₇₄O₁₆P₄Ru: C, 48.70; H, 6.88 %.

4.2.5 Synthesis of *trans*-[Ru(C≡CC₆H₄-4-CN)₂{P(OEt)₃}₄], [**1e**]

A mixture of *trans*-[RuCl₂{P(OEt)₃}₄] (0.21 g, 0.25 mmol), KPF₆ (0.11 g, 0.59 mmol) and HC≡CC₆H₄-4-C≡N (0.076 g, 0.60 mmol) in EtOH (4 ml) and NHⁱPr₂ (2 ml) was stirred under N₂ for 1 month. The solution colour changed from yellow to orange / brown over the reaction period and a white solid precipitated. The reaction solvents were removed under high vacuum, yielding a brown oily residue. The residue was extracted with minimum CH₂Cl₂, filtered through a cotton wool pipette to remove reaction salts and concentrated to dryness by rotary evaporation, yielding an orange / brown oily residue. A minimum amount of MeOH (*ca.* 3 ml) was added to the residue and solution left to in the fridge for 24 hours to aid precipitation of an

orange solid. The orange solid was collected by filtration, washed with minimum cold MeOH (3×3 ml) and air-dried (0.040 g, 19 %). The precipitate may be further purified by recrystallisation from CHCl_3 / MeOH layer diffusion, yielding yellow needles suitable for X-ray crystallography. IR (CH_2Cl_2 , cm^{-1}): 2234 $\nu(\text{C}\equiv\text{N})$, 2219 $\nu(\text{C}\equiv\text{N})$, 2065 $\nu(\text{RuC}\equiv\text{C})$, 1606 $\nu(\text{C}=\text{C})$, 1591 $\nu(\text{C}=\text{C})$. ^1H NMR (CDCl_3 , 300 MHz) δ / ppm: 1.19 (t, $J = 7$ Hz, 36H, CH_3 , $\text{P}(\text{OEt})_3$), 4.25 (quar., $J = 7$ Hz, 24H, CH_2 , $\text{P}(\text{OEt})_3$), 7.01 (d, $J = 8$ Hz, 4H, H^4), 7.37 (d, $J = 8$ Hz, 4H, H^5). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 300 MHz) δ / ppm: 136.8 (s, $\text{Ru}\{\text{P}(\text{OEt})_3\}_4$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 600 MHz) δ / ppm: 16.5 (s, CH_3 , $\text{P}(\text{OEt})_3$), 61.1 (s, CH_2 , $\text{P}(\text{OEt})_3$), 104.9 (s, C^2), 115.1 (s, C^3), 120.4 (s, CN), 130.2 (s, C^4), 131.6 (quin., $J = 20$ Hz, C^1), 131.9 (s, C^5), 135.5 (s, C^6). ESI(+)-MS (m/z): 1019 $[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-C}\equiv\text{N})_2\{\text{P}(\text{OEt})_3\}_4 + \text{H}]^+$.

4.2.6 Synthesis of *trans*- $[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{NO}_2)_2\{\text{P}(\text{OEt})_3\}_4]$, [**1f**]

A mixture of *trans*- $[\text{RuCl}_2\{\text{P}(\text{OEt})_3\}_4]$ (0.10 g, 0.12 mmol), KPF_6 (0.086 g, 0.47 mmol) and $\text{HC}\equiv\text{CC}_6\text{H}_4\text{-4-NO}_2$ (0.044 g, 0.30 mmol) in EtOH (5 ml) and NH^iPr_2 (2 ml) was stirred under N_2 for 24 days. The solution colour changed from orange to brown over the reaction period and a white solid precipitated. The reaction solvents were removed under high vacuum, yielding a dark red oily residue, which was purified by column chromatography (silica, 90 : 10, hexanes : acetone). The first bright red / orange band was collected and solvent removed to yield the product as a bright red precipitate (0.075 g, 59 %). Crystals suitable for single crystal X-ray crystallography were obtained by slow evaporation from CH_2Cl_2 at reduced

temperature ($-18\text{ }^{\circ}\text{C}$). IR (CH_2Cl_2 , cm^{-1}): 2054 $\nu(\text{RuC}\equiv\text{C})$, 1584 $\nu(\text{N}=\text{O})$, 1324 $\nu(\text{N}-\text{O})$. ^1H NMR (CDCl_3 , 600 MHz) δ / ppm: 1.21 (t, $J = 7$ Hz, 36H, CH_3 , $\text{P}(\text{OEt})_3$), 4.25 (quar., $J = 7$ Hz, 24H, CH_2 , $\text{P}(\text{OEt})_3$), 7.03 (d, $J = 9$ Hz, 4H, H^4), 8.02 (d, $J = 9$ Hz, 4H, H^5). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 600 MHz) δ / ppm: 136.2 (s, $\text{Ru}\{\text{P}(\text{OEt})_3\}_4$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 600 MHz) δ / ppm: 16.5 (s, CH_3 , $\text{P}(\text{OEt})_3$), 61.1 (s, CH_2 , $\text{P}(\text{OEt})_3$), 102.2 (quin., $J = 21$ Hz, C^1), 116.9 (s, C^2), 124.0 (s, C^5), 129.9 (s, C^4), 137.9 (s, C^3), 142.8 (s, C^6). ESI(+)-MS (m/z): 1058 $[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-NO}_2)_2\{\text{P}(\text{OEt})_3\}_4]^+$, 953 $[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-NO}_2)\{\text{P}(\text{OEt})_3\}_4 + \text{MeCN}]^+$, 912 $[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-NO}_2)\{\text{P}(\text{OEt})_3\}_4]^+$. Anal. Found: C, 45.46; H, 6.50; N, 2.67. Calc. for $\text{C}_{40}\text{H}_{68}\text{N}_2\text{O}_{16}\text{P}_4\text{Ru}$: C, 45.36; H, 6.48; N, 2.65 %.

4.2.7 Synthesis of *trans*- $[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-C}_5\text{H}_{11})_2\{\text{P}(\text{OEt})_3\}_4]$, [**1g**]

A mixture of *trans*- $[\text{RuCl}_2\{\text{P}(\text{OEt})_3\}_4]$ (0.19 g, 0.22 mmol), KPF_6 (0.14 g, 0.75 mmol) and $\text{HC}\equiv\text{CC}_6\text{H}_4\text{-4-C}_5\text{H}_{11}$ (0.22 ml, 1.13 mmol) in EtOH (5 ml) and NH^iPr_2 (2 ml) was stirred under N_2 for 17 days (or until all *mono*-alkynyl converted to the *bis*-alkynyl complex in solution, monitored by unlocked $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy). The solution colour changed from yellow to orange over the reaction period and a white solid precipitated. The reaction solvents were removed under high vacuum, yielding a brown residue. The residue was extracted with minimum CH_2Cl_2 , filtered through Celite to remove reaction salts and concentrated to dryness by rotary evaporation, yielding a brown residue. A minimum amount of EtOH (2.5 ml) was added to the

residue and solution stirred in an ice bath until a yellow solid separated out (*ca.* 30 minutes). The solid was collected by filtration, washed with minimum cold EtOH (3 × 5 ml) and vacuum dried (0.083 g, 34 %). Large white crystals, suitable for X-ray crystallography, were grown from CDCl₃ / EtOH layer diffusion. IR (CH₂Cl₂, cm⁻¹): 2076 ν(RuC≡C), 1602 ν(C=C). ¹H NMR (CDCl₃, 600 MHz) δ / ppm: 0.89 (t, *J* = 7 Hz, 6H, H¹¹), 1.20 (t, *J* = 7 Hz, 36H, CH₃, P(OEt)₃), 1.29 – 1.37 (m, 8H, H⁸ and H¹⁰), 1.58 (quin., *J* = 7 Hz, 4H, H⁹), 2.51 (t, *J* = 7 Hz, 4H, H⁷), 4.32 (quar., *J* = 7 Hz, 24H, CH₂, P(OEt)₃), 6.92 (d, *J* = 8 Hz, 4H, H⁵), 6.94 (d, *J* = 8 Hz, 4H, H⁴). ³¹P{¹H} NMR (CDCl₃, 300 MHz) δ / ppm: 138.4 (s, Ru{P(OEt)₃}₄). ¹³C{¹H} NMR (CDCl₃, 600 MHz) δ / ppm: 14.2 (s, C¹¹), 16.6 (s, CH₃, P(OEt)₃), 23.0 (s, C⁸ or C¹⁰), 31.3 (s, C⁹), 31.9 (s, C⁸ or C¹⁰), 35.9 (s, C⁷), 61.0 (s, CH₂, P(OEt)₃), 113.5 (s, C²), 114.2 (quin. *J* = 21 Hz, C¹) 127.8 (s, C⁵), 128.9 (s, C³), 129.9 (s, C⁴), 136.9 (s, C⁶). APCI(+)-MS (*m/z*): 1109 [Ru(C≡CC₆H₄-4-C₅H₁₁)₂{P(OEt)₃}₄ + H]⁺, 937 [Ru(C≡CC₆H₄-4-C₅H₁₁){P(OEt)₃}₄]⁺, 771 [Ru(C≡CC₆H₄-4-C₅H₁₁){P(OEt)₃}₃]⁺, 605 [Ru(C≡CC₆H₄-4-C₅H₁₁){P(OEt)₃}₂ + H]⁺. Anal. Found: C, 54.23; H, 8.09. Calc. for C₅₀H₉₀O₁₂P₄Ru: C, 54.13; H, 8.18 %.

4.2.8 Synthesis of *trans*-[Ru(C≡CC₆H₄-4-OMe)₂{P(OEt)₃}₄], [**1h**]

A mixture of *trans*-[RuCl₂{P(OEt)₃}₄] (0.11 g, 0.13 mmol), KPF₆ (0.087 g, 0.47 mmol) and HC≡CC₆H₄-4-OMe (0.3 ml, excess) in EtOH (5 ml) and NHⁱPr₂ (2 ml) was stirred under N₂ for 14 days (or until all *mono*-alkynyl was converted to the *bis*-alkynyl complex in solution, monitored by unlocked ³¹P{¹H} NMR

spectroscopy). The solution colour changed from yellow to orange over the reaction period and a white solid precipitated. The reaction solvents were removed under high vacuum, yielding a brown oily residue. The residue was extracted with minimum CH_2Cl_2 , filtered through Celite to remove reaction salts and concentrated to dryness by rotary evaporation, yielding a brown oil. A minimum amount of MeOH (3 ml) was added to the oily residue, solution stirred for *ca.* two minutes and left in the fridge for *ca.* 1 hour, where a white solid was formed. The solid was collected by filtration, washed with cold MeOH (3×10 ml) and air-dried (0.095 g, 72 %). Crystals suitable for single crystal X-ray crystallography were grown via slow evaporation of a CH_2Cl_2 / hexanes solution. IR (CH_2Cl_2 , cm^{-1}): 2077 $\nu(\text{RuC}\equiv\text{C})$, 1501 $\nu(\text{C}-\text{O})$. ^1H NMR (CDCl_3 , 600 MHz) δ / ppm: 1.20 (t, $J = 7$ Hz, 36H, CH_3 , $\text{P}(\text{OEt})_3$), 3.75 (s, 6H, OCH_3), 4.32 (quar., $J = 7$ Hz, 24H, CH_2 , $\text{P}(\text{OEt})_3$), 6.68 (d, $J = 8$ Hz, 4H, H^4), 6.96 (d, $J = 8$ Hz, 4H, H^5). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 300 MHz) δ / ppm: 138.4 (s, $\text{Ru}\{\text{P}(\text{OEt})_3\}_4$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 600 MHz) δ / ppm: 16.6 (s, CH_3 , $\text{P}(\text{OEt})_3$), 55.3 (s, OCH_3), 61.0 (s, CH_2 , $\text{P}(\text{OEt})_3$), 112.1 (quin., $J = 19$ Hz, C^1), 112.5 (s, C^2), 113.4 (s, C^4), 124.6 (s, C^3), 130.8 (s, C^5), 155.5 (s, C^6). ESI(+)-MS (m/z): 1028 $[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-OMe})_2\{\text{P}(\text{OEt})_3\}_4]^+$, 938 $[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-OMe})\{\text{P}(\text{OEt})_3\}_4 + \text{MeCN}]^+$, 897 $[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-OMe})\{\text{P}(\text{OEt})_3\}_4]^+$. Anal. Found: C, 48.94; H, 7.32. Calc. for $\text{C}_{42}\text{H}_{74}\text{O}_{14}\text{P}_4\text{Ru}$: C, 49.01; H, 7.25 %.

4.3 Crystallography

Following analytical absorption corrections and solution by direct methods, the structures were refined against F^2 with full-matrix least-squares using the program SHELXL-97[64] (**[1b]** and **[1h]**) or SHELXL-2014.[65] All hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic

displacement parameters based on those of the parent atoms. Anisotropic displacement parameters were employed throughout for the non-hydrogen atom. Data have been deposited with the CCDC, reference numbers 1533627-1533633.

4.4 Computational studies

Molecular structure optimizations were performed with the Gaussian 09 program package,[66] using the CAM-B3LYP functional,[67] the LANL2DZ basis set on Ru[68-70] and 6-31G** on all other atoms.[71] A COSMO(CH₂Cl₂) solvent model was applied. Structures were confirmed as true minima by the absence of imaginary frequencies. Molecular orbital analysis was undertaken using the GaussSum package.[72]

5. Supporting Information Available

Plots of the in situ ³¹P NMR spectra from preparation of [**1b**]. Plots of molecules of [**1b-g**] showing the crystallographic numbering schemes and details of structure solution. Tables of crystallographic data.

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