Syntheses and structures of *trans*-bis(alkenylacetylide) ruthenium complexes†

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† Dedicated to Professor T.S. Andy Hor on the occasion of his 65th Birthday and in celebration of his contributions to chemistry and the community.

Abstract

A series of ruthenium alkenylacetylide complexes *trans*-\([\text{Ru}\{\text{C}≡\text{C}(=\text{CH}_2)\text{R}\}\text{Cl}(\text{dppe})_2\}] \quad (\text{R} = \text{Ph} \quad (1\text{a}), \quad \text{C}_4\text{H}_3\text{S} \quad (1\text{b}), \quad 4\text{-MeS}-\text{C}_6\text{H}_4 \quad (1\text{c}), \quad 3,3\text{-dimethyl-2,3-dihydrobenzo}[b]\text{thiophene} \quad (\text{DMBT}) \quad (1\text{d})) or *trans*-\([\text{Ru}\{\text{C}≡\text{C}\text{C}_6\text{H}_9\}\text{Cl}(\text{dppe})_2\}] \quad (1\text{e}) were allowed to react with the corresponding propargylic alcohol \(\text{HC}≡\text{CC}(\text{Me})\text{ROH} \ (\text{R} = \text{Ph} \quad (\text{A}), \quad \text{C}_4\text{H}_3\text{S} \quad (\text{B}), \quad 4\text{-MeS}-\text{C}_6\text{H}_4 \quad (\text{C}), \quad \text{DMBT} \quad (\text{D})) or \text{HC}≡\text{C}\text{C}_6\text{H}_{10}(\text{OH}) \ (\text{E}) in the presence of \text{TIBF}_4 \text{ and DBU to presumably give alkenylacetylide/allenylidene intermediates *trans*-\([\text{Ru}\{\text{C}≡\text{C}(=\text{CH}_2)\text{R}\}\{\text{C}≡\text{C}=\text{C(C(=\text{CH}_2)}\text{Me})\}\text{dppe})_2\}] \quad \text{PF}_6 \quad ([2]\text{PF}_6)]. These complexes were not isolated but deprotonated to give the isolable bis(alkenylacetylide) complexes *trans*-\([\text{Ru}\{\text{C}≡\text{C}(=\text{CH}_2)\text{R}\}_2\text{(dppe)}_2\}] \quad (\text{R} = \text{Ph} \quad (3\text{a}), \quad \text{C}_4\text{H}_3\text{S} \quad (3\text{b}), \quad 4\text{-MeS}-\text{C}_6\text{H}_4 \quad (3\text{c}), \quad \text{DMBT} \quad (3\text{d})) and *trans*-\([\text{Ru}\{\text{C}≡\text{C}\text{C}_6\text{H}_9\}_2\text{(dppe)}_2\}] \quad (3\text{e}). Analogous reactions of *trans*-\([\text{Ru}(\text{CH}_3)_2\text{(dmpe)}_2]\], featuring the more electron-donating 1,2-\text{bis(dimethylphosphino)}\text{ethane} (\text{dmpe}) ancillary ligands, with the propargylic alcohols \text{A} or \text{C} and \text{NH}_4\text{PF}_6 \text{ in methanol allowed isolation of the intermediate mixed alkenylacetylide/allenylidene complexes *trans*-\([\text{Ru}\{\text{C}≡\text{C}(=\text{CH}_2)\text{R}\}\{\text{C}≡\text{C}=\text{C(=\text{CH}_2)}\text{Me})\}\text{dmpe})_2\}] \quad \text{PF}_6 \quad (\text{R} = \text{Ph} \quad ([4\text{a}]\text{PF}_6), \quad 4\text{-MeS}-\text{C}_6\text{H}_4 \quad ([4\text{c}]\text{PF}_6). Deprotonation of \[4\text{a}]\text{PF}_6 \text{ or } [4\text{c}]\text{PF}_6 \text{ gave the symmetric bis(alkenylacetylide) complexes *trans*-\([\text{Ru}\{\text{C}≡\text{C}(=\text{CH}_2)\text{R}\}_2\text{(dmpe)}_2\}] \quad (\text{R} = \text{Ph} \quad (5\text{a}), \quad 4\text{-MeS}-\text{C}_6\text{H}_4 \quad (5\text{c}),) the first of their kind containing the dmpe ancillary ligand sphere. Attempts to isolate bis(allenylidene) complexes \([\text{Ru}\{\text{C}≡\text{C(=\text{CH}_2)}\text{R}\}_2\text{(PP)}_2\}]^{2+} \text{ (PP = dppe, dmpe)} \text{ from treatment of the bis(alkenylacetylide) species } 3 \text{ or } 5 \text{ with } \text{HPB}_4 \text{•Et}_2\text{O were ultimately unsuccessful.}
Introduction

Ruthenium complexes containing trans-bis(alkynyl) ligands are an important and long-standing motif in organometallic chemistry, their structural and electronic properties facilitating study in a diverse range of areas spanning studies of C-C bond forming reactions, molecular-scale electronics, and non-linear optics. In turn, these interests have prompted detailed examination of the electronic structures of these species. Structurally, trans-bis(alkynyl) and closely related trans-bis(polyynyl) complexes of the form \([\text{Ru}\{\text{C}≡\text{C}\}_n\text{R}\}_2\text{L}_n]^{2+}\) may be described in modular terms as a function of their ancillary supporting ligands (comprised of homogenous or heterogenous ligand sets \(\text{L}_4 = (\text{dppe})_2, (\text{dmpe})_2, (\text{dppm})_2, (\text{P(OEt})_3)_4, (\text{CO})_2(\text{PET}_3)_2, 1,5,9,13\text{-tetramethyl-1,5,9,13-tetra-azacyclohexadecane (16-TMC)}^{[10]}\) etc.), the number of C≡C repeat units \(n\) and the terminal substituents \(R\) (Figure 1). Each of these features has been show to exert a significant degree of influence over the electronic structure and corresponding optical, electronic, chemical and electrochemical properties of the complex, giving ample scope to exploit structure-property relationships to design compounds for these various applications. \([3f, 3i, 5c, 5d, 9]\)

![Figure 1](image_url)  
**Figure 1.** Prototypical trans-bis((poly)ynyl) ruthenium complex containing ancillary ligands \(\text{L}_4 = (\text{dppe})_2, (\text{dmpe})_2, (\text{dppm})_2, (\text{P(OEt})_3)_4, (\text{CO})_2(\text{PET}_3)_2, 16\text{-TMC})\).

In contrast to trans-bis((poly)ynyl) ruthenium(II) complexes, trans-bis(cumulene) ruthenium(II) complexes of the general form trans-[\(\text{Ru}\{\text{C}≡\text{C}\}_n\text{R}_2\}_2\text{L}_n]^{2+}\) are rare.\([11]\) Whilst examples of vinylidene, allenylidene\([12]\) and higher cumulene\([14]\) complexes trans-[\(\text{RuCl}\{\text{C}≡\text{C}\}_n\text{R}_2\}_2\text{L}_n]^{+}\) are known, the strongly electron-withdrawing nature of the carbene-
like cumulene ligand decreases the lability of the *trans* chloride ligand making these complexes poor reagents for use in the preparation of substituted derivatives.

Despite the challenges associated with the synthesis of *trans*-bis(cumulene) complexes, these compounds now present as objects of renewed interests following recent studies of the electronic structure and remarkably efficient wire-like properties of organic cumulenes. The electronic structures of cumulene compounds with $C_2$ symmetry have been studied using computational methods, identifying unusual helical molecular orbital topologies induced through molecular orbital torsion.$^{[15]}$ In addition, recent theoretical and experimental studies indicate cumulenes have shallow or even negative conductance decay with molecular length,$^{[16]}$ in direct contrast to the conventional exponential decay in conductance with molecular length observed for polyylnyl and polyenyl molecular wires. The metal centre and ancillary ligands in *trans*-bis(cumulene) complexes provide potential sites to further tune these unusual electronic properties of cumulene compounds. Indeed, preliminary DFT calculations provides further impetus for consideration of bis(cumulene) metal complexes as objects that may offer unusual electronic and optical properties. An analysis of the small model complex *trans*-[$\text{Ru}\{\text{C}=$\text{C}=$\text{C(H)Me}\}(\text{dHpe})_2$]$^{2+}$ reveals a cumulated structure along the length of the 7-atom C=C=Ru=C=C=C chain and helically shaped HOMO, similar to that calculated for the analogous organic [6]cumulene Me(H)C=C=C=C=C=C(H)Me (Figure 2), and prompts further consideration of this class of complex.
Figure 2. The DFT (BLYP35/LANL2DZ(Ru)/6-31G**) optimised structures and plots of the HOMO (contour plotted at ±0.02 \((e/\text{bohr}^3)^{1/2}\)) of the model compounds: (a) trans-\([\text{Ru}\{\text{C} = \text{C} = \text{C}(\text{H})\text{Me}\} (\text{dHpe})]^{2+}\); (b) Me(\text{H})C = C = C = C = C = C(\text{H})Me.

In seeking to identify synthetic routes to bis(cumulene) compounds, the mononuclear ruthenium \textit{trans}-bis(allenylidene) complex \textit{trans}-\([\text{Ru}\{\text{C} = \text{C} = \text{C}(\text{OMe})\text{C} = \text{C}(\text{H})\text{Me}\} (\text{dppm})]_{2}[\text{BF}_4]_{2}\) first reported example by Touchard et al. attracts attention, however this example exhibits a structure more heavily weighted to its alkynyl mesomer (Scheme 1, Figure 3).\footnote{11a} A further survey of crystallographically determined M-C and C-C bond lengths and, in the available examples, molecular orbital structures of examples of bis(allyl) complexes of gold,\footnote{17} silver,\footnote{18} palladium\footnote{19} and platinum,\footnote{19} also suggests the alkynyl mesomer to be favoured in each case (Figure 3).
Scheme 1. Synthesis and resonance forms of Touchard’s putative bis(allenylidene) complex [Ru₂(C=CH(C(OMe)C(H)=CPPh₂)₂(dppm)₂][BF₄]₂.[¹¹]
Reactions of propargylic alcohols with [Rh(η^3-C_3H_5)(P^3Pr_3)_2] or [RhCl(P^3Pr_3)_2] rhodium centres followed by passage through acidic alumina columns have been reported by Werner.
to generate putative bis(allenylidene) intermediates; however isomerisation to more stable $\eta^2$-coordinated hexapentaenylidene complexes arising from coupling of the allenylidene ligands was observed (Scheme 2).[20] A similar process is known to occur for analogous rhodium vinylidene complexes to give coordinated butatrienylidene ligands.[21]

Another early example of a putative bis(allenylidene) complex from Touchard and Dixneuf involves the double oxidation of the trans-bis(ferrocenyl)acetylide precursor $\text{trans-Ru(C≡CFc}_2(\text{dppe})_2$ by two equivalents of ferrocenium, purportedly giving a bis(allenylidene) species, although evidence for its formation is limited solely to infrared analysis with a strong band at 1993 cm$^{-1}$ attributed to the $\nu$(C=C=C) modes (Scheme 3).
Perhaps the most compelling example of a trans-bis(allylidene) complex isolated to date is Rigaut’s trans-[Ru(C≡CPh\textsubscript{2})Cl(dppe)\textsubscript{2}]PF\textsubscript{6} with NaBH\textsubscript{4} resulted in hydride addition to C(γ) to give the acetylide trans-[Ru(C≡C(Ph)\textsubscript{2}H)(dppe)\textsubscript{2}]PF\textsubscript{6}. Treatment of this acetylide species with the propargylic alcohol HC≡CC(Ph)\textsubscript{2}OH gave the allenylidene-acetylide complex trans-[(Ph\textsubscript{2}C=C=C)Ru\{C≡CC(Ph)\textsubscript{2}H\}(dppe)\textsubscript{2}]PF\textsubscript{6}, the mixed ligands giving rise to characteristic ν(C≡C) (2065 cm\textsuperscript{-1}) and ν(C≡C=C) (1919 cm\textsuperscript{-1}) bands in the IR spectrum.

Oxidation of the allenylidene-acetylide complex with Ce(IV) in the presence of KB(C\textsubscript{6}F\textsubscript{5})\textsubscript{4} resulted in hydride elimination, giving the putative bis(allylidene) species trans-[Ru(C≡CPh\textsubscript{2})\textsubscript{2}(dppe)\textsubscript{2}][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}]\textsubscript{2} (ν(C≡C=C): 1923 cm\textsuperscript{-1}) (Scheme 4). Unfortunately, the oxidation step only proceeds cleanly with phenyl substituents, with other groups (R = Me or H) giving a mixture of acetylide and vinylidene isomers.

**Scheme 3.** Ferrocenyl terminated bis(allylidene) complex prepared by Dixneuf et al.\textsuperscript{[5b]}
In searching for a more general route to bis(allenylidene) complexes suited for a wider range of terminal substituents and allowing simple access of $C_2$-symmetric bis(cumulene) species, our attention has been drawn to the recent demonstration of the reversible protonation equilibria of alkenyl acetylide and allenylidene complexes (Scheme 5).\cite{23}

**Scheme 4.** Synthesis of Rigaut’s bis(allenylidene) complex $\text{trans-}[\text{Ru}(\text{C}=\text{CPh}_2)_2(\text{dppe})_2][\text{B}(\text{C}_6\text{F}_5)_4].^{[11b]}$

**Scheme 5.** Schematics showing: (a) the reversible alkenylacetylidyde / methylallenylidene protonation equilibria; (b) electrophilic addition to an alkenylacetylidyde complex yielding a functionalised methyleneallenylidene complex.
The facile interconversion between $\pi$-electron withdrawing allenylidene and strongly $\sigma$-donating / modestly $\pi$-donating acetylide functionalities permits a degree of control over the electronic structure of the ruthenium centre, with the lability of the chloride ligand tuned by this interconversion due to the different trans-effect of the acetylide and allenylidene ligands. In seeking to explore conjugated carbon-rich ligand frameworks, this activation/deactivation of the chloride ligand to substitution reactions with the nature of the trans-ligand, as well as the allenylidene/alkenylacetylide protonation equilibria permits wide scope for the formation of allenylidene and acetylide ligand set combinations.

Results and Discussion

$\textit{trans-}$[Ru{$\textit{C}=\textit{CC}(=\textit{CH}_2)R$}$_2$(dppe)$_2$] Complexes

The methyl allenylidene complexes $\textit{trans-}$[Ru{$\textit{C}=\textit{C}(\textit{Me})R$}Cl(dppe)$_2$]OTf ([1a – e]OTf) were prepared from Selegue-style$^{[24]}$ reactions of the coordinatively unsaturated complex [RuCl(dppe)$_2$]OTf with propargylic alcohols A – E (Scheme 6). Perhaps unsurprisingly, due to the strongly electron withdrawing nature of the $\textit{trans-}$allenylidene ligand which, as noted above, reduces the lability of the chloride ligand, attempts at the formation of bis(allenylidene) complexes from further reaction of [1a – e]OTf with A – E were unsuccessful, even in the presence of strong halide abstractors such as TlBF$_4$ or AgPF$_6$ (Scheme 6).
Scheme 6. A schematic showing the preparation of the monoallenylidene complexes [1a – e]OTf, and unsuccessful attempts at further reactions to generate bis(allenylidene) complexes.

However, deprotonation of the allenylidene complexes [1a – e]OTf to their alkenylacetylide counterparts 1a – e increases the trans-effect and hence the lability of the chloride ligand, and permitted substitution by propargylic alcohols in the presence of TIBF₄ (CARE – Thallium salts are highly toxic).[7, 25] These purple reaction mixtures, presumably contain the mixed acetylide/allenylidene species [{R(Me)C=C=C}Ru{C≡CC(=CH₂)R}(dppe)]BF₄ ([2a – e]BF₄), evidenced by key ³¹P{¹H} NMR resonances at 44.0 ppm and ν(C=C=C) and very weak ν(C≡C) IR bands at ca. 1930 and 2065 cm⁻¹ respectively. These latter vibrational features are consistent with the DFT model [2a⁺] (where the dagger notation is used to distinguish the DFT model from the real complex), which features a strong ν(C=C=C) band at 1941 cm⁻¹ and an extraordinarily weak ν(C≡C) band at 2100 cm⁻¹ (Figure 4).
Figure 4. A summary of important bond lengths (Å) and calculated IR frequencies (scaled by 0.95)$^{[26]}$ from DFT optimised structures of: (a) $[2a]^+$; (b) $3a^+$; (c) $[6a]^+$. These reaction mixtures proved difficult to work up and efforts to isolate examples of these putative intermediates failed, save for $[2a]^+$, which was obtained as the PF$_6^-$ salt by reaction of 1a with A in the presence of NaPF$_6$ in an initial scoping reaction. Rather disappointingly, our attempts to extend this reaction protocol to other examples of complexes $[2]^+$ were unsuccessful. The long reaction times failed to achieve full conversion of other starting materials and the product mixtures proved intractable. Thus despite concerns over toxicity, TlBF$_4$ was chosen as a stronger halide abstractor. In this manner, the addition of DBU to reaction mixtures of $[1a – e]$ with A – E containing TlBF$_4$ after complete reaction (ca. 12
hours) as described above gave the desired bis(alkenylacetylide) complexes by deprotonation of the transiently formed species [2a – e]BF₄ (Scheme 7).

Scheme 7. A proposed reaction scheme illustrating the synthesis of bis(alkenylacetylide) complexes (3a – e), via initial formation and elimination of water from an intermediate hydroxyvinylidene to give the mixed trans-allenylidene/acetylide species ([2a – e]⁺), and deprotonation in situ.

An advantage of the synthetic route shown in Scheme 7 is the versatility with which the terminal substituent R of the propargylic alcohol A – E can be modified, making the synthesis of bis(alkenylacetylide) complexes 3 modular in its scope. In this study, the electroneutral substituents Ph (A) and c₆H₉ (E) were selected, alongside groups R = c₄H₇S (B), 4-MeS-C₆H₄ (C) and 3,3-dimethyl-2,3-dihydrobenzo[b]thiophene (DMBT) (D) that may serve as anchoring groups in future studies of these complexes within molecular junctions.²⁵⁻³⁻

²⁵ The ligand precursor D was prepared in a manner analogous to A,²⁷ by initial lithiation of trimethylsilylacetylene in THF followed by trapping with the carbonyl 1-(2,3-dihydro-3,3-dimethylbenzo[b]thien-5-yl)ethanone. This carbonyl species was in turn prepared via a
modified two-step procedure,\[^{[28]}\] involving first the initial cyclisation of phenylthio-2-methylpropan-2-ol to give 5-ethynyl-3,3-dimethyl-2,3-dihydrobenzo[b]thiophene, followed by Friedel-Crafts acylation using acetyl chloride and AlCl\(_3\), the reaction regioselectively installing an acetyl group para to the thioether group to give 1-(2,3-dihydro-3,3-dimethylbenzo[b]thien-5-yl)ethanone (D) (Scheme 8).

![Scheme 8: Synthesis of 1-(2,3-dihydro-3,3-dimethylbenzo[b]thien-5-yl)ethanone (D).](image)

The two-step reactions affording 3a – e (Scheme 7) typically proceed to completion over the course of 48 hours in CH\(_2\)Cl\(_2\) at room temperature, allowing them to be conveniently tracked by unlocked \(^{31}\)P\(_{1}^{1}\)H NMR spectroscopy (Figure S68). The initial resonances near 50 ppm of 1a – e convert over the course of the reaction via intermediates with resonances near 44 ppm assigned to [2a – e]BF\(_4\) to product resonances at 52 ppm arising from 3a – e. Purification of the crude reaction solutions by elution through a basic alumina column gave the bis(alkenylacetylide) complexes 3a – e in fair to good yields and in high purity.

In the case of reaction of 1e with E, the formation of 3e could be considered to follow an analogous pathway to that proposed for the synthesis of 1e.\[^{[23]}\] The Selegue-style reaction of
propargylic alcohols featuring terminal cyclic substituents afford product mixtures of \(\gamma\)-hydroxyvinlidene and \(\gamma\)-vinylvinylidene upon tele-elimination of water, whilst in each case subsequent deprotonation results in the formation of the desired enynyl ligands and complex 3e (Scheme 9).

Scheme 9. Formation of 3e by deprotonation of allenylidene \([2e]^+\) and \(\gamma\)-vinylvinylidene \([2e']^+\) product mixture formed from water elimination pathways of \(\gamma\)-hydroxyvinlidene, itself formed upon reaction of 1e with E. BF\(_4^-\) anion omitted for clarity.
Complexes 3a – e were identified by the usual suite of spectroscopic methods, including ν(C≡C) bands at ca. 2045 cm$^{-1}$, with a high energy shoulder. These vibrational bands match well with a single conformation of the model system 3a$^\dagger$, which was calculated to feature an asymmetric ν(C≡C) stretch at 2073 cm$^{-1}$ and a weaker shoulder arising from the symmetric ν(C≡C) stretch at 2085 cm$^{-1}$ (Chart 2). A lower energy ν(C≡C) band envelope likely arises from additional conformations of the alkenylacetylide ligands in solution.$^{[29]}$ The cationic molecular ion envelope was also observed in the ESI(+) or APCI(+)−MS spectrum in each case. In addition, resonances at ca. 52.0 ppm characteristic of the trans-bis(acetylide) substituted {Ru(dppe)$_2$} motif in the $^{31}$P{$_1$H} NMR spectra were also observed, as were two geminal proton resonances in the $^1$H NMR spectra at approximately 5.3 and 4.5 ppm, each integrating to two protons with mutual $J_{HH}$ coupling constants from 1.5 – 2.0 Hz.

Single crystals of 3e suitable for X-ray diffraction were obtained, which also supports the formation of the ligand in these bis(alkenylacetylide) species (Figure 5). The terminal cyclohexene substituents were very badly disordered across the 2-fold axis. As such, a rigid body for the cyclohexene was applied, disordered 50:50 about the 2-fold axis, with 3e having two key symmetry independent C≡C bond lengths of 1.183(7) and 1.189(7) Å, consistent with triple bond formation and supporting formation of a trans bis(alkenylacetylide) structure.
Figure 5. A molecule of $3\text{eCH}_2\text{Cl}_2$ showing the atom labelling scheme. Selected hydrogen atoms have been omitted for clarity and thermal ellipsoids are drawn at 50 % probability. Solvent and disorder on the cyclohexene have been removed for clarity. Colour scheme is grey: carbon, pink: phosphorus, white: hydrogen and turquoise: ruthenium.

The crystals which formed when a toluene solution of $3\text{e}$ was allowed to stand for several days were identified by X-ray diffraction as the bis(alkynylketone) species trans-Ru{C≡CC(=O)-4-MeS-C$_6$H$_4$}$_2$(dppe)$_2$ (3c$_{ox}$) (Figure 6). Observation of the molecular ion of this bis(alkynylketone) complex by ESI(+)–MS, as well as a singlet resonance in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 50.05 ppm, the absence of the geminal protons in the $^1\text{H}$ NMR spectrum and a $\nu$(C=O) band at 1579 cm$^{-1}$ further support the proposed structure. The shift in the $\nu$(C≡C) band to lower frequency (2002 cm$^{-1}$) is also consistent with conjugation of the acetylide moiety with the strongly electron withdrawing carbonyl group. The C-O bond length (1.247(3) Å) is typical of carbonyl species, whilst the C1-C2 bond length (1.204(3) Å) further indicates the acetylide functionality is maintained.
Figure 6. A molecule of $3c_{OX}$ with labelling scheme. Hydrogen atoms have been omitted for clarity and thermal ellipsoids drawn at 50%. Colour scheme is grey: carbon, pink: phosphorus, white: hydrogen, red: oxygen, yellow: sulfur and turquoise: ruthenium.

The carbonyl moiety in $3c_{OX}$ is likely formed by radical addition of triplet oxygen to the C=C bond in $3c$, followed by ring opening and elimination of $\text{H}_2\text{C}=\text{O}$ (Scheme 10). Oxidation of organic alkenes resulting in C=C bond cleavage and formation of a carbonyl moiety using $\text{O}_2$ as an oxidant is generally achieved either photo-\cite{30} or thermo-catalytically.\cite{31} Alkene oxidation under catalyst free conditions is currently of interest in organic chemistry,\cite{32} with the formation of $3e$ an unanticipated example of such a process.
Although aerial oxidation of organic alkenes to carbonyls is uncommon, the presence of the ruthenium centre may serve to enhance the electron density in the alkene substituent and accelerate this reaction. This increase in reactivity for alkenylacetylid es has been explored previously for a range of reactive outcomes at C(δ), such as protonation\textsuperscript{[33]} or the addition of carbon-based electrophiles,\textsuperscript{[23]} allowing for the formation of functionalised allenylidene complexes or self-coupled diruthenium vinylidene-alkylidene species such as those previously reported by Selegue.\textsuperscript{[34]}
Table 1. Selected bond lengths (Å) and bond angles (°) from the crystallographically determined structures of 3e and 3cox.

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<th>3cox</th>
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<sup>a</sup>Ru-P max bond length  
<sup>b</sup>Ru-P min bond length

Attempts at the synthesis of unsymmetrically substituted bis(alkenylacetylide) complexes were unsuccessful, with the long reaction times required resulting extensive ligand scrambling and displacement reactions. Thus, reaction of 1c with a small excess of D in the presence of TIBF<sub>4</sub> and DBU gave, albeit over the course of 120 hours, a product distribution containing three key <sup>31</sup>P{<sup>1</sup>H} NMR resonances from 53 – 50 ppm, these corresponding to both symmetric products (3c, 3d) and the mixed ligand compound (Scheme 11, Figure S69). The additional emergence of two sets of triplets at ca. 57 and 52 ppm was also observed, further complicating the product mixture and suggesting further reaction resulting in formation of an additional and as yet unidentified product with cis-dppe ligands, the J<sub>pp</sub> triplet pattern arising due to non-equivalence of the phosphine ligands in the cis-conformation. Rather than a statistical distribution, the product mixture favoured the symmetric complex 3d.
Scheme 11. Ligand scrambling from attempted asymmetric bis(alkenylacetylide) synthesis.

trans-\{Ru\{C≡CC(−CH₂)R\}_2(dmpe)\}_2 Complexes

Given the versatility with which the terminal substituents can be modified using the chemistry summarised in Scheme 7, attention was turned to the ancillary ligand sphere as a means of further tuning the electronic character of these complexes.\[^{36, 31, 10, 35}\] Routes to bis(alkynyl) complexes containing the \{Ru(dmpe)₂\} coordination sphere from reactions of
[Ru(CH$_3$)$_2$(dmpe)$_2$] or [RuH$_2$(dmpe)$_2$] with terminal alkynes in protic solvent are well known.$^{[6, 36]}$ These reactions proceed cleanly through $\sigma$-metathesis of the methyl or hydride ligand with the terminal alkyne, extruding CH$_4$ or H$_2$ respectively. Bis(alkynyl) complexes have also been prepared from the [RuCl$_2$(dmpe)$_2$] precursor by reaction with terminal or silyl protected alkynes, although this necessitated the use of zinc amalgam and high reaction temperatures.$^{[35]}$ Rarer still are examples of ruthenium allenylidene complexes containing the dmpe ancillary ligand. The synthesis of an allenylidene complex from trans-[RuCl$_2$(dmpe)$_2$] and a propargylic alcohol containing a diazafluorenyl substituent via the Selegue route has been reported (Scheme 12),$^{[37]}$ although this required lengthy reaction times at high temperature. The product has been described as being highly susceptible to oxidation whilst in solution, limiting its efficacy for potential application and the extent to which it could be characterised.

![Scheme 12](image)

**Scheme 12.** Synthesis of diazafluorenyl terminated allenylidene complex containing dmpe supporting ligands.$^{[37]}$
In an attempt to circumvent these issues, [Ru(CH$_3$)$_2$(dmpe)$_2$] was reacted directly with propargylic alcohols A – D. Reaction of [Ru(CH$_3$)$_2$(dmpe)$_2$] with 2.5 equivalents of propargylic alcohol A and C in the presence of excess NH$_4$PF$_6$ in methanol resulted in an instant colour change from red to deep purple in both cases. After stirring for three hours, work up afforded the allenylidene-acetylide complexes [4a]PF$_6$ (albeit in low purity) and [4c]PF$_6$ as the dominant products (Scheme 13). Attempts at syntheses using the thiophene and DMBT containing propargylic alcohols B and D were unsuccessful, with only decomposition of the [Ru(CH$_3$)$_2$(dmpe)$_2$] reagent evident in the crude reaction mixtures. The formation of [4a]PF$_6$ and [4c]PF$_6$ may be rationalised in terms of an initial $\sigma$-metathesis of one or both methyl ligands with the propargylic alcohol, followed by proton shuttling from the MeOH solvent or NH$_4^+$ counter ion generating the intermediate vinylidene, allowing tele-elimination of water and subsequent deprotonation of the methylallenylidene ligand. At present it is unclear in what order the sequence of reaction events leading these allenylidene-acetylide mixed-ligand complexes proceed.
Scheme 13. *trans*-allenylidene-acetylide and bis(alkenylacetylide) synthesis containing Ru(dmpe)$_2$ coordination sphere (R = Ph ([4a]PF$_6$ (68 %), 5a (8 %)) and 4-MeS-C$_6$H$_4$ ([4c]PF$_6$ (53 %), 5c (55 %)).

Formation of [4a]PF$_6$ and [4c]PF$_6$ was indicated by the acetylide ν(C≡C) and allenylidene ν(C=C=C) bands at approximately 2050 and 1920 cm$^{-1}$ respectively, similar to those observed for [2a – e]$^+$, a pair of geminal alkene proton resonances in the $^1$H NMR spectra at approximately 5.4 and 5.1 ppm, each integrating to one proton as well as a singlet integrating to three protons at ca. 2.0 ppm corresponding to the methyallenylidene substituent. The $^{31}$P{$^1$H} NMR was especially informative, with these compounds displaying a single resonance near 34 – 35 ppm. The PF$_6^-$ counterion was also observed by both infrared and $^{31}$P{$^1$H} NMR spectroscopies. The isolation of [4a]PF$_6$ and [4c]PF$_6$ supports the notion of the intermediacy of [2a – e]$^+$ in the sequence of reactions leading to the formation of 3a – e from reactions of 1a – e with A – E (c.f. Scheme 7).
Deprotonation of \([4a]\text{PF}_6\) and \([4c]\text{PF}_6\) by treatment with KO\('\text{Bu}\) in THF gave the bis(alkenylacetylide) complexes \(5a\) and \(5c\) (Scheme 13). The \textit{trans}-bis(acetylide) compounds \(5a\) and \(5c\) were readily identified by their characteristic acetylide band \(\nu(\text{C}=\text{C})\) at approximately \(2050\ \text{cm}^{-1}\), and geminal alkene resonances at \(5.3\) and \(4.9\ \text{ppm}\), with mutual \(J_{\text{HH}}\) coupling constants of \(1.6\ \text{Hz}\).

\textit{Towards the synthesis of bis(allenylidene) complexes}

The ready formation of allenylidene complexes \([\text{Ru}\{\text{C}=\text{C}(\text{Me})\text{R}\} \text{(dppe)}\text{Cp}\}^*][\text{BF}_4]\) and \textit{trans}-[\(\text{Ru}\{\text{C}=\text{C}(\text{Me})\text{R}\} \text{Cl}\text{(dppe)}_2][\text{BF}_4]\) from treatment of \([\text{Ru}\{\text{C}≡\text{CC}(\text{=CH}_2)\text{R}\} \text{(dppe)}\text{Cp}\}^*]\) or \textit{trans}-[\(\text{Ru}\{\text{C}≡\text{CC}(\text{=CH}_2)\text{R}\} \text{Cl}\text{(dppe)}_2]\) with HBF\(_4\)\cdot\text{Et}_2\text{O} (c.f. Scheme 5)\(^{23, 33b}\) prompts consideration of the use of bis(alkenylacetylide) complexes as entry points to bis(allenylidene) systems (Scheme 14). The reactions of yellow to orange solutions of \(3a – d\) in CH\(_2\)Cl\(_2\) with HBF\(_4\)\cdot\text{Et}_2\text{O} resulted in the formation of deep blue solutions, with unlocked \(^{31}\text{P}\{^1\text{H}\}\) NMR measurements showing the formation of a transient species at approximately \(42.0\ \text{ppm}\), accompanied by strong IR \(\nu(\text{C}=\text{C})\) bands at ca. \(1930\ \text{cm}^{-1}\). These spectroscopic features have been tentatively assigned to the bis(allenylidene) complexes \textit{trans}-[\(\text{Ru}\{\text{C}=\text{C}(\text{Me})\text{R}\}_2\text{(dppe)}_2][\text{BF}_4]\) \((6a – d)[\text{BF}_4]\). This assignment is supported by calculations with the model complex \([6a]^+\)\(^{2+}\), which gives a strong \(\nu(\text{C}=\text{C})\) band at \(1934\ \text{cm}^{-1}\) (Chart 2).

Unfortunately, upon standing the colour of these solutions gradually reverts to purple and the resonance at \(42.0\ \text{ppm}\) diminishes, followed by formation of the allenylidene-acetylide complexes \([2]^+\), indicated by the emergence of resonances at ca. \(44\ \text{ppm}\) together with additional unidentified resonances at ca \(45 – 46\ \text{ppm}\), with a corresponding decrease in
intensity of the bis(allenylidene) resonance in the unlocked $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. The emergence of a resonance at ca. 41 ppm within the product mixture presumably corresponding to the mono-methylallenylidene $[1]^+$ is also observed, suggesting cleavage of a single alkynyl ligand has also occurred. Infrared spectra of these solutions are in accordance with the reformation of $[1]^+$ and $[2]^+$, containing strong $\nu(\text{C}=$C$=$C) bands at ca 1930 cm$^{-1}$, and very weak $\nu(\text{C}=$C$)$ bands at ca. 2065 cm$^{-1}$.

Scheme 14. Schematic representation of attempts to generate bis(allenylidene) complexes ($[6\text{a} - \text{d}]^{2^+}$) by protonation of bis(alkenylacetylide) complexes $3\text{a} - \text{d}, 5\text{a,c}$.}

In contrast to the reactions of $3\text{a} - \text{d}$ described above, treatment of $3\text{e}$ with HBF$_4$$\cdot$Et$_2$O resulted in the formation of a 1:1 product mixture likely corresponding to allenylidene-
acetylide $[2e]^+$ and vinylvinylidene-acetylide $[2e]^+$ products (Scheme 8), evidenced by $^{31}\text{P}\{^1\text{H}\}$ resonances at 40.24 and 40.05 ppm and accompanying vinylidene $\nu(\text{C}=$C) and allenylidene $\nu(\text{C}=$C=$\text{C})$ IR bands at 1625 and 1957 cm$^{-1}$ respectively. This is in accordance with Selegue’s observed allenylidene/vinylvinylidene formation equilibria from the protonation of enynyl complexes containing cyclic terminal substituents,$^{[33a]}$ as well as more recent observations from our group.$^{[23]}$

Although $5a$ and $5c$ contain more electron donating dmpe ancillary ligands and might be viewed as being able to better support the ruthenium centre with two strongly back-bonding allenylidene ligands, treatment of either of these complexes with HBF$_4$Et$_2$O resulted in formation of unidentified mixtures of a large number of products. Whilst $[4a,c]\text{PF}_6$ are generated under mildly acidic conditions with NH$_4$PF$_6$ as a reagent, protonation of these species to give the bis(allenylidene) is not observed under these reaction conditions. Efforts to generate the putative bis(allenylidene) by direct protonation of $[4a,c]^+$ using the stronger acid HBF$_4$Et$_2$O were also unsuccessful.

**Conclusions**

A modular synthesis of bis(alkenylacetylide) complexes based on the $\{\text{Ru(dppe)}_2\}$ and $\{\text{Ru(dmpe)}_2\}$ fragments has been developed. Whilst this approach permits modification of both terminal substituents and the ancillary ligand sphere, attempts at synthesis of bis(allenylidene) complexes from these precursors was ultimately unsuccessful. The relatively high acidity of the terminal methyl protons and strongly electron withdrawing character of the allenylidene ligands ultimately favours formation of allenylidene-acetylide or bis(alkynyl) tautomers in these systems. Such options are not available in the case of the Rigaut complex trans-$[\text{Ru(C}=$C=$\text{CPh}_2)_2(\text{dppe})_2]^2+$ and which remains one of the few well-defined examples of a complex of this type. The presence of terminal functional groups
capable of serving as contacting groups to metal electrodes makes 3b – d, 4c and 5c appealing candidates for incorporation within a molecular junction, which will be the subject of future efforts.

**Experimental**

**General conditions**

All reactions were performed under an atmosphere of nitrogen employing standard Schlenk techniques in oven-dried glassware. For the dppe-containing compounds 1 – 3, no particular care was taken to exclude air upon work-up of reaction products, whilst dmpe containing compounds [4]PF₆ and 5 were handled and stored under inert conditions. Solvents were dried by literature methods or by an Innovative Technologies Solvent Purification System and sparged with nitrogen before use. For chromatography, silica gel was used as received and alumina (basic) was oven dried (100 °C) overnight before use.

The compounds HC≡CC(OH)(Me)R (R = Ph,[27] 4-MeS-C₆H₄,[27] C₄H₃S,[38] DMBT,[28]), [RuCl(dppe)₂]OTf,[39] RuCl₂(PPh₃)₃,[39] trans-[Ru{CC≡C(CH₂)(R)}Cl(dppe)₂] (R = Ph,[23] C₄H₃S,[23] 4-MeS-C₆H₄[23]), [RuCl(dppe)₂]OTf,[39] trans-[RuCl₂(dmpe)₂][6b] and trans-[Ru(CH₃)₂(dmpe)₂][36b] were prepared either in accordance with, or with slight refinements to existing literature procedures. All other chemicals were purchased and used as received.

The various ¹H, ¹³C{¹H}, ³¹P{¹H} and ¹⁹F{¹H} spectra were recorded on a Varian 400 MHz (¹H: 399.86 MHz, ¹³C: 100.6 MHz, ³¹P: 161.9 MHz), Bruker 400 MHz (¹H: 400.13 MHz, ¹³C: 100.6 MHz, ³¹P: 161.9 MHz, ¹⁹F{¹H} 376.5 MHz) Bruker 500 MHz (¹H: 500.10 MHz, ¹³C: 125.8 MHz, ³¹P: 202.4, ¹⁹F{¹H}: 470.4 MHz) and Bruker 600 MHz (¹H: 600.10 MHz, ¹³C: 150.9 MHz, ³¹P: 242.9, ¹⁹F{¹H}: 564.7 MHz) spectrometers at room temperature. Chemical shifts in ¹H and ¹³C{¹H} spectra are reported relative to the residual protio solvent.
Unless stated otherwise $^{31}\text{P}\{^1\text{H}\}$ and $^{19}\text{F}\{^1\text{H}\}$ chemical shifts are reported relative to the NMR spectrometer lock signal. The relaxation agent $[\text{Cr(acac)}_3]$ was used during the acquisition of $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the allenylidene complex [1d]OTf in order to resolve the $C(\alpha)$, $C(\beta)$ and $C(\gamma)$ resonances. For all NMR spectra, multiplets are reported according to their closest first order approximation. For all NMR assignments, $H_o$, $H_m$ and $H_p$ refer to the ortho, meta and para protons of the phenyl rings of the ancillary phosphine ligands respectively, whilst $C_i$, $C_o$, $C_m$, $C_p$, similarly refer to the ipso, ortho, meta and para carbons of these same phenyl rings. IR spectra were recorded on an Agilent Cary 630 FTIR Spectrometer using ATR or in transmission mode from solutions between CaF$_2$ plates. Mass Spectra were obtained from a Waters Liquid Chromatograph Premier Mass Spectrometer, using positive mode Electrospray Ionisation (ESI(+)) or Atmospheric Pressure Chemical Ionisation (APCI(+)). Samples were prepared in MeCN or MeOH and inserted by direct injection via the on-board injector.

**Single crystal X-ray diffraction analysis.** Crystallographic data for the structures were collected on a XtaLAB Synergy, Single source at home/near, HyPix diffractometer. The crystals were kept at a 101 K during data collection. Both structures were solved with the ShelXT 2018/2 solution program using dual methods and by using Olex2 1.3 as the graphical interface. The model was refined with XL using full matrix least squares minimisation on $F^2$. Anisotropic displacement parameters were employed for the non-hydrogen atoms. 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 atom. For crystal 3e CH$_2$Cl$_2$, the cyclohexene ligands were modelled using a rigid body, disordered 50:50 about a 2-fold axis. Copies of the data with CCDC numbers 2098240 and 2098241 can be obtained free of charge via [https://www.ccdc.cam.ac.uk/structures/](https://www.ccdc.cam.ac.uk/structures/), or from the Cambridge
Density Functional Theory (DFT) calculations

Calculations were carried out using the GAUSSIAN09 (revision A.02)\cite{46} and results analysed with the aid of the GaussView5.0 and GaussSum3.0\cite{47} suite of programs. Geometry optimisations and frequency calculations employed the BLYP35 functional\cite{48} with the LANL2DZ\cite{49} basis set for ruthenium and 6-31G**\cite{50} for all other atoms. All optimised structures were confirmed as true minima through the absence of imaginary frequencies. Reported values of vibrational frequencies have been scaled by a factor of 0.95.\cite{26}

\begin{center}
\includegraphics[width=0.2\textwidth]{molecule.png}
\end{center}

\textit{Synthesis of phenylthio-2-methyl-propan-2-ol}

An acetone solution (120 mL) of thioanisole (2.80 mL, 27.32 mmol) and 2,2-dimethyloxirane (2.45 mL, 27.59 mmol) were sparged under N$_2$ for 20 minutes. NEt$_3$ (9 mL) was added and the reaction mixture stirred for 24 hours. Solvent was removed under reduced pressure, giving the product as a pale yellow oil, which was sufficiently pure for further use (4.9 g, 27 mmol, 97 %). $^1$H NMR (CDCl$_3$ 500 MHz) $\delta$ / ppm: 7.44 (d, $J_{HH} = 7.3$ Hz, 2H, H$_3$); 7.33 – 7.29 (m, 2H, H$_3$); 7.21 (t, $J_{HH} = 7.3$ Hz, 1H, H$_1$); 3.15 (s, 2H, CH$_2$); 2.24 (s, 1H, OH); 1.33 (s, 6H, 2 x CH$_3$). $^{13}$C\{$_1$H\} NMR (CDCl$_3$ 125.8 MHz) $\delta$ / ppm: 137.1 (s, C$_4$); 129.7 (s, C$_3$); 129.1 (s, C$_2$); 126.4 (s, C$_1$); 70.9 (s, C(CH$_3$_)$_2$); 48.7 (s, CH$_2$); 28.8 (s, CH$_3$).
Synthesis of 2,3-dihydro-3,3-dimethylbenzo[b]thiophene (DMBT)

A CH₂Cl₂ (120 mL) solution of AlCl₃ (10.5 g, 78.7 mmol) was charged with phenylthio-2-methyl-propan-2-ol (2.4 g, 13.2 mmol) and stirred under refluxing conditions for 3 hours. The solution was cooled to 0 °C and cautiously quenched with 5 % HCl (100 mL). The aqueous layer was extracted with CH₂Cl₂ (2 × 100 mL) and the combined organic layers then washed with 5 % NaHCO₃ (100 mL) and brine (100 mL), dried over MgSO₄ and filtered. Solvent was removed by rotary evaporator, giving a dark yellow oil, which was subsequently purified by eluting through a silica plug with n-hexane. Removal of solvent gave a pale yellow oil (1.3 g, 7.9 mmol, 60 %). ¹H NMR (CDCl₃ 400 MHz) δ / ppm: 7.20 –7.18 (m, 1H, Hₘₐᵢₜ); 7.14 – 7.10 (m, 1H, Hₘₐᵢₜ); 7.07 – 7.05 (m, 2H, Hₘₐᵢₜ); 3.18 (s, 2H, CH₂); 1.38 (s, 6H, 2 × CH₃).

¹³C{¹H} NMR (CDCl₃ 100.6 MHz) δ / ppm: 148.0 (s, Cₘₐᵢₜ); 140.5 (s, Cₘₐᵢₜ); 127.5 (s, Cₘₐᵢₜ); 124.6 (s, Cₘₐᵢₜ); 122.8 (s, Cₘₐᵢₜ); 122.5 (s, Cₘₐᵢₜ); 47.4 (s, C(CH₃)₂); 47.3 (s, CH₂); 27.5 (s, 2 x CH₃).

Synthesis of 1-(2,3-dihydro-3,3-dimethylbenzo[b]thien-5-yl)ethanone (Acetyl DMBT)

A CH₂Cl₂ solution of AlCl₃ (3.30 g, 24.1 mmol) was slowly charged with 2,3-dihydro-3,3-dimethylbenzo[b]thiophene (2.60 g, 15.8 mmol) and acetyl chloride (1.30 mL, 18.2 mmol) and stirred for 2 hours at room temperature. The reaction mixture was then cooled to 0 °C and cautiously quenched with water (100 mL). The aqueous layer was extracted with Et₂O (4 × 50 mL), after which the combined organic extracts were washed with 5 % NaHCO₃ (100 mL) and brine (100 mL), dried over MgSO₄ and filtered. Removal of solvent gave a crude yellow oil that was purified by a silica column, using n-hexane/Et₂O (1:1) as the eluent, giving a yellow oil (1.9 g, 9.0 mmol, 57 %). ¹H NMR (CDCl₃ 400 MHz) δ / ppm: 7.72 (dd, JHH = 1.6,
8.1 Hz, 1H, H\textSUB{Ar}, DMBT); 7.65 (d, \(J_{HH} = 1.6\) Hz, 1H, H\textSUB{Ar}, DMBT); 7.24 (d, \(J_{HH} = 8.1\) Hz, 1H, H\textSUB{Ar}, DMBT); 3.23 (s, 2H, CH\textSUB{2}); 2.56 (s, 3H, (C=O)CH\textSUB{3}); 1.41 (s, 6H, 2 \times \text{Me of DMBT}).

\(^{13}\text{C}\{^1\text{H}\} \text{ NMR (CDCl}_3 100.6\text{ MHz}) \delta / \text{ppm: 197.4 (s, C=O); 148.8 (s, C_{quaternary, DMBT}); 148.2 (s, C_{quaternary, DMBT}); 134.2 (s, C_{quaternary, DMBT}); 128.6 (s, C_{Ar, DMBT}); 122.3 (s, C_{Ar, DMBT}); 122.1 (s, C_{Ar, DMBT}); 47.6 (s, CH\textSUB{2}); 47.2 (s, C(CH\textSUB{3})\textSUB{2}); 27.6 (s, 2 \times \text{Me of DMBT}); 26.7 \(9\) (s, (C=O)CH\textSUB{3}). IR ATR \nu / \text{cm}^{-1}: 1672 \nu(C=O).

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=0.5\textwidth]{image}};
\end{tikzpicture}
\end{center}

**Synthesis of HC≡CC(Me)DMBTOH (D)**

A THF solution (50 mL) of HC≡CSiMe\textSUB{3} (1.9 mL, 13.5 mmol) was cooled to -78 °C. \textit{n}-BuLi (2.5 M in \textit{n}-hexane) (5.4 mL, 13.5 mmol) was added and the reaction mixture stirred for 1 hour. 1-(2,3-dihydro-3,3-dimethylbenzo[b]thien-5-yl)ethanone (1.8 g, 8.9 mmol) was added and the reaction mixture stirred at -78 °C for one hour before the temperature was allowed to rise to room temperature. The reaction mixture was stirred for a further 48 hours, after which it was quenched with NH\textsubscript{4}Cl solution (100 mL) and the organic layer extracted with EtOAc (2 x 50 mL). The combined organic extracts were washed with brine (50 mL), dried over MgSO\textsubscript{4} and filtered. Solvent was removed by rotary evaporator, leaving a crude yellow oil (2.6 g). This was added with K\textsubscript{2}CO\textsubscript{3} (0.71 g, 5.4 mmol) to MeOH (40 mL) and stirred overnight. NH\textsubscript{4}Cl (30 mL) was added and the product extracted with EtOAc (2 x 30 mL), after which the combined organic extracts were washed with brine (30 mL), dried over MgSO\textsubscript{4} and filtered. Solvent was removed by rotary evaporator, leaving the product as a crude yellow oil. Purification (silica chromatography) gave the product as a yellow oil (1.1 g, 4.7 mmol, 53 %). \(^1\text{H} \text{ NMR (CDCl}_3 500 \text{ MHz}) \delta / \text{ppm: 7.42 (dd, } J_{HH} = 1.9, 8.1 \text{ Hz, 1H, H}_{Ar, DMBT}); 7.35 (d, } J_{HH} = 1.9 \text{ Hz, 1H, H}_{Ar, DMBT}); 7.16 (d, } J_{HH} = 8.1 \text{ Hz, 1H, H}_{Ar, DMBT});
3.19 (s, 2H, CH₂); 2.67 (s, 1H, H₁); 2.32 (s, 1H, OH); 1.78 (s, 3H, H₄); 1.39 (s, 3H, Me of DMBT); 1.38 (s, 3H, Me of DMBT). ¹³C{¹H} NMR (CDCl₃ 125.8 MHz) δ / ppm: 148.3 (s, C₉ quaternary, DMBT); 141.8 (s, C₃); 140.5 (s, C₉ quaternary, DMBT); 128.6 (s, C₉ Ar, DMBT); 124.5 (s, C₉ Ar, DMBT); 122.2 (s, C₉ Ar, DMBT); 119.3 (s, C₉ Ar, DMBT); 87.5 (s, C₂); 73.2 (s, C₁); 47.6 (s, CH₂, DMBT); 47.5 (s, C(CH₃)₂, DMBT); 33.3 (s, C₄); 27.52 (s, Me of DMBT); 27.50 (s, Me of DMBT). IR ATR ν / cm⁻¹: 3423 ν(OH); 3287 ν(C≡CH); 2110 ν(C≡C). ESI(+)-MS m/z: Calculated for [M]⁺ ([C₁₄H₁₆OS]⁺) = 232.0922. Observed: 233.1000 [M + H]⁺; 215.0894 [M – OH]⁺.

**Synthesis of trans-[Ru{C=C=C(Me)DMBT}Cl(dppe)₂]OTf ([1d]OTf)**

A CH₂Cl₂ solution (40 mL) of [RuCl(dppe)₂]OTf (0.41 g, 0.38 mmol) and D (0.16 g, 0.60 mmol) was stirred for 48 hours. Solvent was removed under reduced pressure, the residue dissolved in minimal CH₂Cl₂ and precipitated by the addition of Et₂O (50 mL), giving a purple powder, which was collected by vacuum filtration and washed with n-hexane (2 × 10 mL) (0.48 g, 0.37 mmol, 98 %). ¹H NMR (CDCl₃ 400 MHz) δ / ppm: 7.35 – 7.32 (m, 1H, DMBT); 7.29 – 7.24 (m, 10H, dppe); 7.14 – 7.01 (m, 30H, dppe); 6.72 (d, J_HH = 8.3 Hz, 1H, DMBT); 6.48 (d, J_HH = 8.3 Hz, 1H, DMBT); 6.48 (d, J_HH = 8.3 Hz, 1H, DMBT); 3.20 (s, 2H, CH₂ of DMBT), 3.04 (m, 4H, dppe); 2.79 (m, 4H, dppe); 1.74 (s, 3H, H₄); 1.30 (s, 6H, 2 × Me of DMBT). ¹³C{¹H} NMR (CDCl₃ 100.6 MHz) δ / ppm: 296.4 (m, C₁); 197.9 (s, C₂); 162.4 (s, C₃); 151.0 (s, C₉ quaternary, DMBT); 149.7 (s, C₉ quaternary, DMBT); 140.1 (s, C₃); 134.6 – 134.5 (m, Cᵢ, dppe); 133.9 – 133.8 (m, Cₒ, dppe); 133.4 – 133.3 (m, Cₒ, dppe); 131.2 (s, Cᵢ, dppe); 130.4 (s, Cᵢ, dppe); 129.3 (C₉ Ar, DMBT); 128.7 (m, Cₚ, dppe); 127.9 (m, Cₚ, dppe); 123.0 (s, C₉ Ar, DMBT); 122.2
(s, C<sub>Ar</sub>, DMBT); 47.9 (s, C(CH<sub>3</sub>)<sub>2</sub> of DMBT); 47.1 (s, CH<sub>2</sub> of DMBT); 31.3 (s, C<sub>4</sub>); 29.2 (m, dppe); 27.6 (s, 2 × Me of DMBT). ¹³P{¹H} NMR (CDCl<sub>3</sub> 161.9 MHz) δ / ppm: 41.26 (s, dppe). ¹⁹F{¹H} NMR (CDCl<sub>3</sub> 376.5 MHz) δ / ppm: -77.93 (s, OTf). IR ATR ν / cm⁻¹: 1927 ν(C=C=C); 1262 ν(OTf). ESI(+)−MS m/z: Calculated for [M]<sup>+</sup> ([C<sub>66</sub>H<sub>62</sub>ClP<sub>4</sub>SRu]<sup>+</sup>) = 1147.2255. Observed: 1147.2272 [M]<sup>+</sup>.

**Synthesis of trans-[Ru{C≡CC(=CH<sub>2</sub>)DMBT}Cl(dppe)]<sub>2</sub> (1d)**

A THF solution (40 mL) of [1d]OTf (0.45 g, 0.35 mmol) and t-BuOK (0.05 g, 0.45 mmol) was stirred for 2 hours. Solvent was removed under reduced pressure and the residue eluted through a short basic alumina plug with CH<sub>2</sub>Cl<sub>2</sub>. Solvent was removed by rotary evaporator, giving the product as a yellow-green powder (0.32 g, 0.28 mmol, 79%). ¹H NMR (CDCl<sub>3</sub> 400 MHz) δ / ppm: 7.67 – 7.65 (m, 4H, H<sub>o</sub>, dppe); 7.19 – 7.13 (m, 8H, H<sub>p</sub>, dppe); 7.08 – 7.06 (m, 4H, H<sub>o</sub>, dppe); 6.99 – 6.94 (m, 16H, H<sub>m</sub>, dppe); 6.93 – 6.92 (m, 1H, DMBT); 6.85 (d, J<sub>HH</sub> = 8.0 Hz, 1H, DMBT); 6.82 (dd, J<sub>HH</sub> = 1.5, 8.0 Hz, 1H, DMBT); 5.17 (app d, J<sub>HH</sub> = 2.1 Hz, 1H, H<sub>4a/b</sub>); 4.69 (App d, J<sub>HH</sub> = 2.1 Hz, 1H, H<sub>4a/b</sub>); 3.08 (s, 2H, CH<sub>2</sub>, DMBT); 2.75 (m, 4H, dppe); 2.59 (m, 4H, dppe); 1.14 (s, 6H, 2 × Me of DMBT). ¹³C{¹H} NMR (CDCl<sub>3</sub> 100.6 MHz) δ / ppm: 147.4 (s, C<sub>quaternary</sub>, DMBT); 139.2 (s, C<sub>3</sub>); 138.5 (s, C<sub>quaternary</sub>, DMBT); 136.8 – 136.6 (m, C<sub>i</sub>, dppe); 135.8 – 135.6 (m, C<sub>i</sub>, dppe); 134.9 – 134.8 (m, C<sub>o</sub>, dppe); 134.6 – 134.5 (m, C<sub>1</sub>); 134.3 – 134.2 (m, C<sub>o</sub>, dppe); 129.2 (s, C<sub>p</sub>, dppe); 129.0 (s, C<sub>2</sub>); 128.87 (s, C<sub>p</sub>, dppe); 127.5 – 127.4 (m, C<sub>m</sub>, dppe); 127.0 – 126.9 (m, C<sub>m</sub>, dppe); 126.6 (s, C<sub>Ar</sub>, DMBT); 121.7 (s, C<sub>Ar</sub>, DMBT); 120.9 (s, C<sub>Ar</sub>, DMBT); 114.8 (s, C<sub>3</sub>); 111.7 (s, C<sub>4</sub>); 47.6 (s, CH<sub>2</sub>, DMBT); 47.1 (s, C(CH<sub>3</sub>)<sub>2</sub>, DMBT); 31.0 – 30.5 (m, dppe); 27.3 (s, 2 × Me of DMBT).
$^{31}$P{$^1$H} NMR (CDCl$_3$ 161.9 MHz) $\delta$ / ppm: 49.27 (s, dppe). IR ATR $\nu$ / cm$^{-1}$: 2052 $\nu$(C≡C).


**Synthesis of trans- [{Ph(Me)C=C=C}Ru{CCC(=H)$_2$}Ph](dppe)$_2$PF$_6$ ([2a]PF$_6$)**

A CH$_2$Cl$_2$ solution (30 mL) of 1a (0.21 g, 0.20 mmol), A (0.057 g, 0.39 mmol) and NaPF$_6$ (0.069 g, 0.41 mmol) was stirred for 24 hrs, resulting in a gradual colour change from red to purple. Solvent was removed under reduced pressure, the residues dissolved in minimal CH$_2$Cl$_2$ and filtered into Et$_2$O. Collection by filtration and washing with n-hexane (2 x 10 mL) gave [2a]PF$_6$ as a purple/black powder (0.25 g, 0.19 mmol, 90%). $^1$H NMR (CDCl$_3$ 600 MHz) $\delta$ / ppm: 7.37 – 6.88 (m, 50H, dppe + Ph); 5.53 (m, 1H, H$_{4a/b}$); 5.00 (m, 1H, H$_{4a/b}$); 3.02 (m, 4H, dppe); 2.92 (m, 4H, dppe); 1.79 (s, 3H, H$_{4'}$). $^{13}$C{$^1$H} NMR (CDCl$_3$ 150.9 MHz) $\delta$ / ppm: 205.7 (m, C$_1$); 164.3 (s, C$_2$); 142.2 (s, C$_3$); 140.3, 134.2, 133.8, 133.3 131.2, 130.5, 129.3, 128.7, 128.6, 127.6 (s, Ph); 138.1 (m, C$_o$, dppe); 135.5 (m, C$_o$, dppe); 133.7 (m, C$_o$, dppe); 132.8 (m, C$_m$, dppe); 130.8 (s, C$_p$, dppe); 130.3 (s, C$_p$, dppe); 129.0 (m, C$_{1'}$); 128.5 (m, C$_m$, dppe); 128.1 (m, C$_m$, dppe); 126.7 (s, C$_{2'}$); 116.4 (s, C$_{4'}$); 31.1 (s, C$_4$); 30.2 – 30.0 (m, dppe). $^{31}$P{$^1$H} NMR (CDCl$_3$ 242.9 MHz) $\delta$ / ppm: 44.42 (s, dppe); -144.20 (sept., PF$_6$).

IR(CH$_2$Cl$_2$) $\nu$ / cm$^{-1}$: 2075 $\nu$(C≡C); 1931 $\nu$(C=C). PF$_6$ band obscured by solvent. ESI(+)-MS $m/z$: Calculated for [M]$^+$ ([C$_{66}$H$_{61}$ClP$_4$SRu]$^+$) = 1153.2924 Observed: 1153.2982. [M]$^+$.

*Bis(alkenylacetylilde) synthesis*
**WARNING:** TlBF$_4$ is used in the following reactions. This compound is highly toxic and as such, urgent care must be taken with its use. Appropriate care and controls were employed to minimise all risks associated with its use and all thallium salts generated in subsequent reactions were disposed of appropriately. Gloves, weighing paper and chromatographic alumina used in its handling were all disposed of in a labelled thallium waste container.

**General procedure for synthesis of bis(alkenylacetylide) complexes**

The appropriate alkenylacetylide 1a – e, propargylic alcohol A – E (2 equiv) and TlBF$_4$ (2 equiv) were stirred overnight in CH$_2$Cl$_2$ (30 mL), and which time DBU (5 drops) was added and the mixture stirred for a further 72 hours. Solvent was removed and the residue filtered through a basic alumina plug with CH$_2$Cl$_2$ (3 cm) to remove Tl$^+$ salts. Solvent was removed by rotary evaporator and the product washed with $n$-hexane (2 × 10 mL).

**Synthesis of trans-[Ru{C≡CC(=CH$_2$)Ph}$_2$(dppe)$_2$] (3a)**

Prepared from trans-Ru{C≡CC(=CH$_2$)Ph}Cl(dppe)$_2$ (1a) (0.14 g, 0.14 mmol), HC≡CC(OH)(Ph)Me (A) (0.05 g, 0.35 mmol) and TlBF$_4$ (0.09 g, 0.29 mmol) in the manner described above. Workup gave the product as an orange-yellow powder (0.075 g, 0.065 mmol, 48 %). $^1$H NMR (CDCl$_3$ 500 MHz) δ / ppm: 7.44 (m, 16H, dppe); 7.15 – 7.06 (m, 18H, Ph); 6.87 (t, J = 7.63 Hz, 16H, H$_m$, dppe); 5.23 (app d, J = 2.0 Hz, 2H, H$_{4a/b}$); 4.66 (app d, J = 2.0 Hz, 2H, H$_{4a/b}$); 2.64 (m, 8H, dppe). $^{13}$C{$^1$H} NMR (CDCl$_3$, 125.8 MHz) δ / ppm: 141.8 (s; C$_5$); 137.2 (m, C$_i$, dppe); 136.2 (s, Ph); 134.4 (m, C$_o$, dppe); 132.2 (t, $J_{CP} = 15.3$ Hz, C$_1$); 128.7 (s, C$_p$, dppe); 127.7 (s, Ph); 127.2 (m, C$_m$, dppe); 126.9 (s, Ph); 126.5 (s,
C\textsubscript{3}; 116.6 (s, C\textsubscript{5}); 112.3 (s, C\textsubscript{4}); 31.3 – 31.2 (m, dppe). \textsuperscript{31}P{\textsuperscript{1}H} NMR (CDCl\textsubscript{3}, 202.4 MHz) \(\delta\) / ppm: 53.02 (s, dppe). IR ATR / \(\nu\) cm\textsuperscript{-1}: 2045 \(\nu\) (C≡C). APCI(+) - MS \(m/z\): Calculated for [M]\textsuperscript{+} ([C\textsubscript{72}H\textsubscript{62}P\textsubscript{4}Ru\textsubscript{7}]\textsuperscript{+}) = 1152.2845. Observed: 1153.2910 [M + H]\textsuperscript{+}.

\begin{center}
\includegraphics[width=0.5\textwidth]{structure1}
\end{center}

\textit{Synthesis of trans-[Ru\{C≡C(−CH\textsubscript{2})−2−C\textsubscript{4}H\textsubscript{5}S\}\textsubscript{2}(dppe)\textsubscript{2}] (3b)}

Prepared from trans-Ru\{C≡CC(−CH\textsubscript{2})−2−C\textsubscript{4}H\textsubscript{5}S\}Cl(dppe)\textsubscript{2} (1b) (0.35 g, 0.33 mmol), HC≡CC(OH)(−2−C\textsubscript{4}H\textsubscript{5}S)Me (B) (0.15 g, 0.99 mmol) and TlBF\textsubscript{4} (0.20 g, 0.69 mmol) in the manner described above, with the exception the reaction was stirred instead for 72 hours. Workup gave the product as a red brown powder (0.21 g, 0.18 mmol, 55 %). \textsuperscript{1}H NMR (CDCl\textsubscript{3} 400 MHz) \(\delta\) / ppm: 7.64 – 7.44 (m, 16H, H\textsubscript{o}, dppe); 7.12 (t, \(J_{HH}\) = 7.4 Hz, 8H, H\textsubscript{p}, dppe); 6.99 (dd, \(J_{HH}\) = 1.2, 5.0 Hz, 2H, H\textsubscript{6/8}); 6.91 (t, \(J_{HH}\) = 7.6 Hz, 16H, H\textsubscript{m}, dppe); 6.68 (dd, \(J_{HH}\) = 3.5, 5.0 Hz, 2H, H\textsubscript{7}); 6.42 (dd, \(J_{HH}\) = 1.2, 3.5 Hz, 2H, H\textsubscript{6/8}); 5.25 (m, 2H, H\textsubscript{4a/b}); 4.45 (m, 2H, H\textsubscript{4a/b}); 2.69 (m, 8H, dppe). \textsuperscript{13}C{\textsuperscript{1}H} NMR (CDCl\textsubscript{3} 100.6 MHz) \(\delta\) / ppm: 146.6 (s, C\textsubscript{5}; 137.2 – 136.8 (m, C\textsubscript{i}, dppe); 134.6 – 134.5 (m, C\textsubscript{i}, dppe); 134.4 – 134.3 (m, C\textsubscript{o}, dppe); 132.9 – 132.6 (m, C\textsubscript{4}); 128.7 (s, C\textsubscript{p}, dppe); 128.2 (s, C\textsubscript{2}); 127.3 (m, C\textsubscript{m}, dppe); 127.0 (s, C\textsubscript{7}); 124.8 (s, C\textsubscript{6/8}); 123.1 (s, C\textsubscript{6/8}); 115.6 (s, C\textsubscript{3}); 111.4 (s, C\textsubscript{4}); 31.3 – 31.1 (m, dppe). \textsuperscript{31}P{\textsuperscript{1}H} NMR (CDCl\textsubscript{3} 161.9 MHz) \(\delta\) / ppm: 52.06 (s, dppe). IR ATR / \(\nu\) cm\textsuperscript{-1}: 2046 \(\nu\) (C≡C). ESI(+) - MS \(m/z\): Calculated for [M]\textsuperscript{+} ([C\textsubscript{68}H\textsubscript{58}P\textsubscript{4}RuS\textsubscript{2}]\textsuperscript{+}) = 1164.1974. Observed: 1165.2024 [M + H]\textsuperscript{+}.

\begin{center}
\includegraphics[width=0.5\textwidth]{structure2}
\end{center}
Synthesis of trans-[Ru\{C≡CC(=CH_2)-4-SMe-C_6H_4\}_2(dppe)_2] (3c)

Prepared from trans-Ru\{C≡CC(=CH_2)-4-MeS-C_6H_4\}Cl(dppe)_2 (1c) (0.15 g, 0.14 mmol), HC≡CC(OH)(-4-MeS-C_6H_4)Me (C) (0.053 g, 0.28 mmol) and TIBF_4 (0.080 g, 0.28 mmol) in the manner described above. Workup gave the product as a red-orange powder (0.12 g, 0.096 mmol, 71 %). ^1H NMR (CDCl_3 400 MHz) δ / ppm: 7.43 – 7.41 (m, 16H, H_o, dppe); 7.10 (t, J_{HH} = 7.3 Hz, 8H, H_p, dppe); 7.02 (app d, J_{HH} = 8.4 Hz, 4H, H_6/7); 6.91 (app d, J_{HH} = 8.4 Hz, 4H, H_6/7); 6.87 (t, J_{HH} = 7.6 Hz, 16H, H_m, dppe); 5.24 (app d, J_{HH} = 1.6 Hz, 2H, H_4a/b); 4.69 (app d, J_{HH} = 1.6 Hz, 2H, H_4a/b); 2.66 (m, 8H, dppe); 2.45 (s, 6H, SMe). ^13C{^1H} NMR (CDCl_3, 125.8 MHz ) δ / ppm: 138.8 (s, C_5), 137.2 (m, C_i, dppe); 134.3 (m, C_o, dppe); 128.7 (s, C_p, dppe); 127.3 (s, C_6/7); 127.2 (m, C_m, dppe); 126.4 (s, C_6/7); 116.4 (s, C_3); 111.6 (s, C_4); 31.2 (m, dppe); 16.5 (s, SMe). (C(α) and C(β) not observed). ^31P{^1H} NMR (CDCl_3 161.9 MHz) δ / ppm: 52.51 (s, dppe). IR ATR / ν cm⁻¹: 2041 ν(C≡C). ESI(+)-MS m/z: Calculated for [M]^+ ([C_{74}H_{66}P_4RuS_2]^+) = 1244.2600. Observed: 1245.2681 [M]^+.

![Chemical Structure](image)

Synthesis of trans-[Ru\{C≡CC(=CH_2)DMBT\}_2(dppe)_2] (3d)

Prepared from trans-Ru\{C≡CC(=CH_2)DMBT\}Cl(dppe)_2 (1d) (0.30 g, 0.26 mmol), HC≡CC(OH)(DMBT)Me (D) (0.11 g, 0.47 mmol) and TIBF_4 (0.16 g, 0.54 mmol) in the manner described above, with the exception the reaction was stirred instead for 72 hours. Workup gave the product as a yellow powder (0.15 g, 0.11 mmol, 44 %). ^1H NMR (CDCl_3 400 MHz) δ / ppm: 7.41 – 7.39 (m, 16H, H_o, dppe); 7.17 (d, J_{HH} = 8.1 Hz, 2H, DMBT); 7.09 (t, J_{HH} = 7.3 Hz, 8H, H_p, dppe); 6.94 (d, J_{HH} = 1.4 Hz, 2H, DMBT); 6.90 (dd, J_{HH} = 1.4, 8.1 Hz, 2H, DMBT); 6.87 – 6.83 (m, 16H, H_m, dppe); 5.21 (app d, J_{HH} = 1.5 Hz, 2H, H_4a/b); 4.71
(app d, $J_{HH} = 1.5$ Hz, 2H, H$_{4a/b}$); 3.06 (s, 4H, CH$_2$, DMBT); 2.66 (m, 8H, dppe); 1.08 (s, 12H, CH$_3$, DMBT). $^{13}$C {$^1$H} NMR (CDCl$_3$ 100.6 MHz) $\delta$ / ppm: 147.3 (s, C$_{\text{quaternary}}$, DMBT); 139.1 (s, C$_5$); 138.4 (s, C$_{\text{quaternary}}$, DMBT); 137.5 – 137.2 (m, C$_i$, dppe); 136.4 (s, C$_2$); 134.4 – 134.3 (m, C$_o$, dppe); 132.2 – 131.7 (m, C$_1$); 128.7 (s, C$_p$, dppe); 127.2 – 127.1 (m, C$_m$, dppe); 126.5 (s, Ar-H, DMBT); 121.7 (s, C$_{Ar}$, DMBT); 121.3 (s, C$_{Ar}$, DMBT); 117.0 (s, C$_3$); 111.4 (s, C$_4$); 47.6 (s, CH$_2$, DMBT); 47.0 (s, C(CH$_3$)$_2$, DMBT); 31.4 – 31.3 (m, dppe); 27.1 (s, Me of DMBT). $^{31}$P {$^1$H} NMR (CDCl$_3$ 161.9 MHz) $\delta$ / ppm: 51.43 (s, dppe).

IR ATR $\nu$ / cm$^{-1}$: 2046 $\nu$(C≡C).

ESI(+)-MS m/z: Calculated for [M]$^+$ ([C$_{80}$H$_{74}$P$_4$S$_2$Ru]$^+$) = 1324.3226. Observed: 1325.3317 [M + H]$^+$.

\[
\begin{array}{c}
\text{C} - \text{C} - \text{C} - \text{Ru} - \text{C} - \text{C} - \text{C} \\
\text{Ph}_2\text{P} \quad \text{Ph}_2\text{P}
\end{array}
\]

**Synthesis of trans-[Ru{C≡C(C≡CH)(=CH$_2$)$_4$}$_2$(dppe)$_2$] (3e)**
Prepared from trans-Ru{C≡C(C≡CH)(=CH$_2$)$_4$}Cl(dppe)$_2$ (1e) (0.35 g, 0.34 mmol), HC≡C–C$_6$H$_{10}$(OH) (E) (0.087 g, 0.70 mmol) and TiBF$_4$ (0.20 g, 0.69 mmol) in the manner described above. Workup gave the product as a yellow-brown powder (0.16 g, 0.15 mmol, 43%). Crystals suitable for X-ray diffractometry were grown by layering a solution of 2e in CH$_2$Cl$_2$ with $n$-hexane. $^1$H NMR (CDCl$_3$ 400 MHz) $\delta$ / ppm: 7.51 – 7.49 (m, 16H, H$_o$); 7.16 (t, $J = 7.3$ Hz, 8H, H$_p$); 6.96 (t, $J = 7.6$ Hz, 16H, H$_m$); 5.14 (m, 2H, H$_4$); 2.58 (m, 8H, dppe); 2.06 (m, 4H, CH$_2$); 1.76 (m, 4H, CH$_2$); 1.55 (m, 8H, CH$_2$). $^{13}$C {$^1$H} NMR (CDCl$_3$ 100.6 MHz) $\delta$ / ppm: 137.8 – 137.6 (m, C$_i$, dppe); 134.6 (m, C$_o$, dppe); 128.4 (s, C$_p$, dppe); 127.2 (m, C$_1$); 126.9 (m, C$_m$, dppe); 126.4 (s, C$_2$); 123.0 (s, C$_3$); 118.5 (s, C$_4$); 31.8 – 31.5 (m, dppe); 30.4 (s, CH$_2$); 25.9 (s, CH$_2$); 23.4 (s, CH$_2$); 22.8 (s, CH$_2$). $^{31}$P {$^1$H} NMR (CDCl$_3$ 161.9 MHz) $\delta$ / ppm: 53.76 (s, dppe). IR ATR / $\nu$ cm$^{-1}$: 2049 $\nu$(C≡C). ESI(+)-MS m/z: Calculated for [M]$^+$ ([C$_{68}$H$_{66}$P$_4$Ru]$^+$) = 1108.3158. Observed: 1108.3164 [M]$^+$. 

39
trans-\([\text{Ru}\{\text{C}≡\text{C}=\text{O}\}-\text{4-MeS-C}_{8}\text{H}_{4}\}_{2}(\text{dppe})_{2}]\) (3cox)

Obtained as yellow crystals from a solution of 2c in toluene left to stand over the course of several days. No attempts to exclude air or moisture were made during this period. $^1$H NMR (CDCl$_3$ 400 MHz) $\delta$ / ppm: 7.35 – 7.30 (m, 20H, H$_o$ + H$_s$); 7.07 (t, $J_{HH} = 7.4$ Hz, 8H, H$_p$); 6.90 (t, $J_{HH} = 7.6$ Hz, 16H, H$_m$); 6.83 (app d, $J_{HH} = 8.5$ Hz, 4H, H$_e$); 2.94 (m, 8H, dppe); 2.47 (s, 6H, SMe). $^{13}$C{${}^1$H} NMR (CDCl$_3$ 100.6 MHz) $\delta$ / ppm: 174.1 (s, C$_3$); 142.8 (s, C$_4$); 136.1 (m, C$_i$, dppe); 135.7 (s, C$_7$); 133.9 (m, C$_o$, dppe); 133.6 (m, C$_i$, dppe); 130.9 (m, C$_1$); 129.9 (s, C$_3$); 129.4 (s, C$_p$); 128.4 (s, C$_2$); 127.6 (m, C$_m$, dppe); 124.5 (s, C$_o$); 31.4 (m, dppe); 15.2 (s, SMe). $^{31}$P{${}^1$H} NMR (CDCl$_3$ 161.9 MHz) $\delta$ / ppm: 50.05 (s, dppe). IR ATR $\nu$ / cm$^{-1}$: 2002 $\nu$(C≡C); 1579 $\nu$(C=O). ESI(+)-MS $m/z$: Calculated for [M + H]$^+$ ([C$_{72}$H$_{63}$P$_4$O$_2$S$_2$Ru]$^+$) = 1249.2263. Observed: 1249.2292 [M + H]$^+$.  

**Synthesis of trans-[RuCl$_2$(dmpe)$_2$]**

A solution of dmpe (1.6 mL, 9.4 mmol) in acetone (100 mL) was transferred via cannula to a Schlenk flask containing RuCl$_2$(PPh$_3$)$_3$ (3.7 g, 3.8 mmol) and stirred under refluxing conditions for 4 hours. The solution was then cooled and filtered under an inert atmosphere of N$_2$. Solvent was removed under reduced pressure giving a yellow solid. This was washed with n-hexane (3 x 20 mL) and dried under vacuum to give the product as a pale yellow
powder (1.3 g, 2.7 mmol, 71%). $^1$H NMR (CDCl$_3$ 400 MHz) $\delta$ / ppm: 1.62 – 1.58 (m, 8H, dmpe); 1.45 (s (br), 24H, P-CH$_3$). $^{13}$C{$^1$H} NMR (CDCl$_3$ 100.6 MHz) $\delta$ / ppm: 29.6 – 29.1 (m, dmpe); 12.7 – 12.4 (m, P-CH$_3$). $^{31}$P{$^1$H} NMR (CDCl$_3$ 161.9 MHz) $\delta$ / ppm: 39.00 (s, dmpe).


![Chemical structure](image)

**Synthesis of trans-[Ru(CH$_3$)$_2$(dmpe)$_2$]**

A solution of RuCl$_2$(dmpe)$_2$ (3.0 g, 6.4 mmol) in benzene (100 mL) was charged with MeLi (14.0 mL, 22.4 mmol) and stirred for 48 hours. Solvent was removed under reduced pressure and the residue extracted with $n$-pentane (3 x 50 mL) under an inert atmosphere of N$_2$. Solvent was removed under reduced pressure, giving the product as a pale green powder (1.3 g, 3.0 mmol, 47%). Decomposition under air was observed after several hours, necessitating storage and handling under inert conditions. $^1$H NMR (CDCl$_3$ 400 MHz) $\delta$ / ppm: 1.50 – 1.45 (m, 8H, dmpe); 1.23 (s, 24H, P-CH$_3$); -1.63 (s (br), 6H, Ru-CH$_3$). $^{13}$C{$^1$H} NMR (CDCl$_3$ 100.6 MHz) $\delta$ / ppm: 29.7 (m, dmpe); 14.8 (m, P-CH$_3$); -25.2 (m, Ru-CH$_3$). $^{31}$P{$^1$H} NMR (CDCl$_3$ 161.9 MHz) $\delta$ / ppm: 46.65 (s, dmpe). APCI(+)-MS $m/z$: Calculated for [M]$^+$ ([(C$_{14}$H$_38$P$_4$Ru)$^+$) = 432.0967. Observed: 458.0981 [M – CH$_3$ + MeCN]$^+$.

**Synthesis of trans-alkynyl/allenylidene complexes**
Synthesis of trans-[Ru{C≡C≡C(Me)-4-MeS-C₆H₄}{C≡CC(=CH₂)Ph}(dmpe)₂]PF₆ ([4a]PF₆)

A MeOH solution (10 mL) of Ru(CH₃)₂(dmpe)₂ (0.16 g, 0.36 mmol), A (0.13 g, 0.89 mmol) and NH₄PF₆ (0.20 g, 1.2 mmol) was stirred for four hours, giving a deep purple solution. Solvent was filtered under an inert N₂ atmosphere and solvent removed under reduced pressure. The residue was dissolved in a minimum amount of CH₂Cl₂ and precipitated by addition to Et₂O (100 mL). A purple solid was collected by vacuum filtration and dried under vacuum, giving the product as a purple powder (0.2 g, 0.24 mmol, 68%).

1H NMR (CDCl₃ 400 MHz) δ / ppm: 7.94 – 7.22 (m, 10H, Ph); 5.30 (m, 1H, H₄a/b); 5.12 (m, 1H, H₄a/b); 2.02 (s, 3H, H₄); 1.93 – 1.81 (m, 8H, dmpe); 1.63 (s, 12H, P-CH₃); 1.44 (s, 12H, P-CH₃).

13C{¹H} NMR (CDCl₃ 100.6 MHz) δ / ppm: 208.1 (m, C₁); 159.5 (s, C₂); 141.8 (s, C₃); 139.0, 134.1, 133.0, 128.3, 128.1, 128.0, 127.9 127.8, 126.32 (s, Ph); 114.3 (s, C₄); 130.0 (s, C₃'); 32.5 (s, C₄); 29.9 – 29.3 (m, dmpe); 17.4 – 17.2 (m, P-CH₃); 15.6 – 15.5 (m, P-CH₃) C₁' and C₂' not observed; allenylidene carbon resonances inferred from ¹H-¹³C{¹H} HMBC spectrum.

3¹P{¹H} NMR (CDCl₃ 161.9 MHz) δ / ppm: 34.22 (s, dmpe); 144.28 (sept, PF₆). IR ATR ν / cm⁻¹: 2064 ν(C≡C); 1917 ν(C≡C-C). APCI(+)-MS m/z: Calculated for ([C₃₂H₄₇P₄Ru]⁺) [M]⁺ = 657.1672. Observed: 657.1665 [M]⁺.
Synthesis of trans-[Ru\{C=C(C(\text{Me})=\text{C}-4-\text{MeS}-\text{C}_6\text{H}_4\}\{\text{C}=\text{CC(-CH)}_2-4-\text{MeSC}_6\text{H}_4\}\{\text{dmpe}\}_2]\text{PF}_6 ([4\text{c}]\text{PF}_6)

A MeOH solution of Ru(CH$_3$)$_2$(dmpe)$_2$ (0.15 g, 0.35 mmol), C (0.15 g, 0.78 mmol) and NH$_4$PF$_6$ (0.20 g, 1.2 mmol) were stirred for four hours, giving a deep purple solution. Solvent was filtered under an inert N$_2$ atmosphere and solvent removed under reduced pressure. The residue was dissolved in a minimum amount of CH$_2$Cl$_2$ and precipitated by addition to Et$_2$O (100 mL). A purple solid was collected by vacuum filtration and dried under vacuum, giving the product as a purple powder (0.17 g, 0.19 mmol, 53%).

$^1$H NMR (CDCl$_3$ 400 MHz) δ / ppm: 7.84 (d, J$_{HH} = 8.4$ Hz, 2H, C$_6'$/7'); 7.54 (d, J$_{HH} = 8.1$ Hz, 2H, C$_6'$/7'); 7.21 – 7.19 (m, 4H, C$_6$+C$_7$); 5.46 (m, 1H, H$_4'$a/b); 5.06 (m, 1H, H$_4'$a/b); 2.55 (s, 3H, SMe); 2.50 (s, 3H, SMe); 2.05 (s, 3H, H$_4'$a); 1.94 (m, 8H, dmpe); 1.62 (s, 12H, P-$\text{CH}_3$); 1.45 (s, 12H, P-$\text{CH}_3$).

$^{13}$C\{$^1$H\} NMR (CDCl$_3$ 100.6 MHz) δ / ppm: 200.5 (m, C$_1$); 159.4 (s, C$_2$); 148.3 (s, C$_3$); 142.9 (s, C$_5$); 139.3 (s, C$_5$); 138.0 (s, C$_8$); 136.8 (s, C$_3$); 133.4 (s, C$_8$); 128.6 (s, C$_6'/7'$); 126.7 (s, C$_6'/7'$); 126.2 (s, C$_6'/7'$); 126.0 (s, C$_5'/7'$); 113.4 (s, C$_4'$); 31.5 (s, C$_4$); 29.8 (m, dmpe); 17.3 (m, P-CH$_3$); 15.9 (s, SMe); 15.5 (m, P-CH$_3$); 14.7 (s, SMe). C$_1$- and C$_2'$ not observed. $^{31}$P\{$^1$H\} NMR (CDCl$_3$ 161.9 MHz) δ / ppm: 34.75 (s, dmpe); 144.28 (sept, PF$_6$). IR ATR ν / cm$^{-1}$: 2065 ν(C=\text{C}); 1915 ν(\text{C}=\text{C}). ESI(+)-MS m/z: Calculated for ([C$_3$H$_5$P$_4$S$_2$Ru]$^+$) [M]$^+$ = 749.1426. Observed: 749.1451 [M]$^+$.

Bis(alkenylacetylide) synthesis

General procedure for synthesis of bis(alkenylacetylide) complexes

Solutions of [4a,c]PF$_6$ and KOtBu were stirred in THF for 4 hours. Solvent was removed and the solution filtered through a Celite plug (2.5 cm), eluting with CH$_2$Cl$_2$. Removal of solvent and drying under vacuum gave the title compounds 5a,c.
Synthesis of trans-[Ru{C≡CC(=CH₂)Ph}₂(dmpe)] (5a)

Prepared from [4a]PF₆ (0.15 g, 0.19 mmol) and KO'Bu (0.051 g, 0.46 mmol) in the manner described above. The complex 5a was obtained as a bright orange powder (0.025 g, 0.038 mmol, 8%). ¹H NMR (CDCl₃ 400 MHz) δ / ppm: 7.72 (d, J₆H₇ = 7.3 Hz, 2H, H₆/7); 7.23 (d, J₆H₇ = 7.7 Hz, 2H, H₆/7); 7.18 (t, J₆H₇ = 7.3, 7.7 Hz, 1H, H₈); 5.33 (app d, J₄a/b = 1.7 Hz, 2H, H₄a/b); 4.98 (app d, J₄H₄ = 1.7 Hz, 2H, H₄a/b); 1.69 (m, 8H, dmpe); 1.55 (s, 24H, P–CH₃).

¹³C{¹H} NMR (CDCl₃ 100.6 MHz) δ / ppm: 141.2 (s, C₅); 127.6 (s, C₆/7); 126.8 (s, C₈); 126.6 (s, C₆/7); 109.7 (s, C₄); 30.6 – 30.4 (m, dmpe); 16.4 (m, P-CH₃). Other carbons not detected.

³¹P{¹H} NMR (CDCl₃ 161.9 MHz) δ / ppm: 41.4 (s, dmpe). IR ATR ν / cm⁻¹: 2040 ν(C≡C).

ESI(+) MS m/z: Calculated for ([C₃₂H₄₆P₄Ru⁺]⁺ [M⁺]⁺ = 656.1593. Observed: 657.1588 [M + H⁺]⁺.

Synthesis of trans-[Ru{C≡CC(=CH₂)4-MeS-C₆H₄}₂(dmpe)] (5c)

Prepared from [4c]PF₆ (0.12 g, 0.13 mmol) and KO'Bu (0.035 g, 0.31 mmol) in the manner described above. The complex 5c was obtained as a red/orange powder (0.055 g, 0.074 mmol, 55%). ¹H NMR (CDCl₃ 400 MHz) δ / ppm: 7.65 (app d, J₆H₇ = 8.4 Hz, 4H, H₆/7); 7.14 (app d, J₆H₇ = 8.4 Hz, 4H, H₆/7); 5.30 (app d, J₄H₄ = 1.6 Hz, 2H, H₄a/b); 4.94 (app d, J₄H₄ =
1.6 Hz, 2H, H$_{4a/b}$); 2.47 (s, 6H, SMe); 1.69 (m, 8H, dmpe); 1.54 (s, 24H, P-CH$_3$). $^{13}$C{$^1$H} NMR (CDCl$_3$ 100.6 MHz) δ / ppm: 138.3 (s, C$_{5/8}$); 136.5 (s, C$_{5/8}$); 134.7 (s, C$_3$); 127.0 (s, C$_{6/7}$); 126.1 (s, C$_{6/7}$); 109.2 (s, C$_4$); 30.6 – 30.4 (m, dmpe); 16.5 – 16.3 (m, P-CH$_3$); 16.2 (s, SMe) (C(α) and C(β) not observed). $^{31}$P{$^1$H} NMR (CDCl$_3$ 161.9 MHz) δ / ppm: 41.36 (s, dmpe). IR ATR ν / cm$^{-1}$: 2040 ν(C≡C). ESI(+)-MS m/z: [M]$^+$ ([C$_{34}$H$_{50}$P$_4$S$_2$Ru]$^+$) = 748.1348. Observed: 749.1451 [M + H]$^+$. 

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**Keywords**

acetylide; allenylidene; cumulene; helical molecular orbitals; Ruthenium

**References**


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In seeking to prepare ruthenium bis(allenylidene) complexes as examples of metal compounds displaying helically structured frontier molecular orbitals, bis(alkenylacetylide) complexes were investigated as potential synthetic precursors. A modular synthesis was devised allowing facile manipulation of the ancillary ligand sphere and terminal substituents. Whilst some evidence for the formation of bis(allenylidene) complexes was obtained, these complexes remain elusive. However the wealth of unusual chemistry displayed by the bis(alkenylacetylide) complexes sign-post future opportunities for further exploration of these carbon-rich ligand systems.

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