Some ruthenium derivatives of penta-1,4-diyn-3-one

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The complex \( \{\text{Ru(dppe)Cp}^*\}C\equiv C\)\(\text{C}_2\text{CO} \) serves as an entry point to a range of bimetallic complexes linked by cross-conjugated bridging ligands bearing a pendant group, \( E \). The extent of \( \pi \)-delocalisation between the metal centers through the cross-conjugated ligand appears to be sensitive to the electronic nature of \( E \).
Abstract
The reaction between Ru(C≡CH)(dppe)Cp* 1 and oxalyl chloride affords \(\{\text{Ru(dppe)Cp*}\}C≡C_2\text{CO}\ 2\) in 72% yield. Methylation (MeOTf) of 2 occurs firstly on the carbonyl oxygen, affording \(\{\text{Ru(dppe)Cp*}\}C≡C_2\text{C(OMe)}\)OTf [3]OTf. A second methylation of [3]+ on the alkynyl C\(\beta\), proceeds slowly, affording \(\{\text{Cp*(dppe)Ru}\}\text{CMeC(OMe)CC(Ru(dppe)Cp*)}\)OTf [4][OTf]2, whereas protonation of [3]+ occurs readily to give crystallographically characterized \(\{\text{Cp*(dppe)Ru}\}\text{CCHC(OMe)CC(Ru(dppe)Cp*)}\)OTf [5][OTf]2. The molecular structures of [3]OTf and [5][OTf]2 suggest that polarization by the CO group results in significant contributions from the alkynyl-allenylidene or alkynyl-carbyne mesomers, respectively. Reaction of 2 in refluxing MeOH containing \[\text{NH}_4\]PF\(_6\) results in partial methanolysis to give Ru\{C≡CC(OMe)CH=CH\}C(OMe)C(dppe)Cp* 6. Knövenagel condensation of 2 with CH\(_2\)(CN)\(_2\) affords \(\{\text{Ru(dppe)Cp*}\}C≡C_2\text{C}=\text{C(CN)}_2\ 7\). The related asymmetric complex \(\{\text{Cp*(dppe)Ru}\}C≡\text{C}[\text{C=C(CN)}_2]\text{C}=\text{C=C(Ru(dppe)Cp*)}\) 8 was obtained from the reaction between Ru\{C≡CC(CN)=C(CN)\}_2\}C(dppe)Cp* and lithiated Ru(C≡CC=C)(dppe)Cp*. Single crystal structural determinations of 2, [3]OTf, [5][OTf]2, 6, 7 and 8 are reported, together with a supporting computational study of relevant electronic structures.
Introduction

The highly unsaturated molecule penta-1,4-diyne-3-one, or bis(ethynyl)ketone, (HC≡C)₂CO was first reported in 1933. A variety of synthetic routes to this material and derivatives are now known, with one common approach to bis(alkynyl) ketones involving reactions of a formic ester with alkynyllithium reagents, followed by oxidation of the resulting alcohols, (RC≡C)₂CH(OH). The latter step is often achieved with K₂Cr₂O₇ or MnO₂, exemplified in the syntheses of (Me₃SiC≡C)₂CO² and (FcC≡C)₂CO.³,⁴ Alternative approaches include reaction of an alkynoic chloride, RC≡CC(O)Cl with Me₃SiC≡C≡CC≡SiMe₃ under Friedel-Crafts conditions to give RC≡CC(O)C≡CC≡CSiMe₃, for example.³⁻⁵ However, to the best of our knowledge, there are only three derivatives of the ‘skipped diyne’ penta-1,4-diyne-3-one which contain transition metals, namely FeC≡CC(O)C≡CSiPr₃,² (FcC≡C)₂CO³,⁴ and {(Ph₃P)AuC≡C}₂CO.⁵

The range of complexes in which two metal-ligand fragments are linked by unsaturated bridges, particularly -(C≡C)ₓ- chains,⁶ has recently been expanded to include compounds in which other groups, including a third metal-ligand moiety, such as ferrocene and biferrocene,⁷,⁸ Ru(dppe)₂⁹ Ru₂(DMBA)₄ (DMBA = N,N’-dimethylbenzamidinate),¹⁰ C₂O₂(CO)₂(dppe),¹¹ Pd(PEt₃)₂,¹² and Hg,¹³ and also transition metal clusters,¹⁴ have been inserted into the π-conjugated pathway. There is much current interest in the electronic structures of these complexes, and both experimental and computational results suggest that the inserted group may act as an insulator or an amplifier, with respect to the extent of π-conjugation between the metal end-groups.⁷⁻⁹,¹³,¹⁵⁻¹⁹

We and others have also studied the effect of inserting a variety of organic groups,¹⁵ particularly aromatic hydrocarbon and heterocyclic systems, into the carbon chain of complexes \{LₙM\}(C≡C)ₓ{MLₙ}, on the electronic interactions between the end-groups.²⁰⁻²⁵ The metal end-groups are often strongly electron-donating in character, such as M(dppe)Cp* (M = Fe, Ru) and the formal insertion of electron-attracting groups, such as CO, C=CH₂, C=C(CN)₂, into the bridge is a natural extension of this work, whilst also allowing further exploration of bimetallic complexes featuring cross-conjugated, carbon-rich ligands.¹¹,¹⁵,²⁶ The increasing awareness of the role that
quantum interference (QI) effects may play in determining the transport of charge through molecules and proposals for QI-driven single molecule transistors based on cross-conjugated scaffolds add further interest to development of methods for the preparation of such cross-conjugated systems and the chemistry appropriate for tuning the relative lengths of the various \( \pi \)-channels. This paper describes our work on the syntheses, characterization and properties of the dimetalla-ethynyl ketone \( \{ \text{Cp*(dppe)Ru}\}C=\text{C} \text{C} \text{C} \text{O} \) and some related compounds.
Results and Discussion

Metalla-desilylation of trimethylsilyl-alkynes or -polyynes is an efficient route to alkylnyl- or polyynyl-metal complexes.\(^{29}\) However, the attempted metalla-desilylation of (Me\(_3\)SiC≡C)\(_2\)CO with RuCl(PP)Cp' [(PP)Cp' = (PPh\(_3\))\(_2\)Cp, (dppe)Cp, (dppe)Cp*] using a range of conditions (KF, [NBu\(_4\)]F or NaOMe),\(^{29,30}\) in the presence of salts of large anions ([NH\(_4\)]PF\(_6\), Na[BPh\(_4\)]), additional bases (NEt\(_3\), dbu) and in various solvents (MeOH, Bu'OH, thf) proved unsuccessful, only recovered starting material or RuH(PP)Cp' (from reaction of the chloro complex with alcohols / bases\(^{31}\)) having been obtained. It is likely that the presence of the electron-withdrawing ketone function deactivates the deprotected (HC≡C)\(_2\)CO (which is also unstable under these reaction conditions) towards metallation. Transmetalation of (PPh\(_3\)AuC≡C)\(_2\)CO with RuCl(dppe)Cp was also examined,\(^{32}\) but this led to the formation of an unusual dimetal-substituted pyrylium complex [1,3-{Ru(dppe)Cp}]\(_2\){c-COC(OMe)CHCCH}]PF\(_6\),\(^5\) rather than the desired bimetallic complex {[Cp(dppe)Ru]C≡C}\(_2\)CO.

Recently, it has been noted that the ethynyl complexes Ru(C≡CH)(PP)Cp' are strong nucleophiles, reacting with tetracyanoethene, for example, with elimination of HCN and formation of the corresponding tricyanovinylethynyl complexes, Ru{C≡CC(CN)=C(CN)}\(_2\)C{C≡CH}C{C≡C}(CN)\(_2\)CO,\(^{33}\) rather than undergoing the usual [2 + 2]-cycloaddition and subsequent ring-opening reactions to form tetracyanobutadienyl derivatives, Ru{C≡CC(CN)=C(CN)}\(_2\)CH-C{C≡C}(CN)\(_2\)C{C≡C}(CN)\(_2\)CO.\(^{34}\) Unfortunately, reactions of Ru(C≡CH)(dppe)Cp* 1 with ketonic precursors, such as bis(2,4-bisnitrophenyl)oxalate,\(^{35}\) diethyl carbonate or bis(imidazolyl) ketone, did not afford the desired compounds, even under relatively harsh conditions (refluxing THF for 3 d).

Interestingly, reactions of 1 with oxalyl dichloride followed by treatment with NEt\(_3\) were discovered to yield the desired bis(metalla-ethynyl)ketone, ({Cp*}(dppe)Ru}C≡C)\(_2\)CO 2. Scale-up and optimisation of the reaction conditions led to isolation of 2 in 72% yield (Scheme 1). Complex 2 is a yellow solid which was initially characterized by elemental analysis and mass spectrometry, with confirmation of the molecular structure being achieved with a single-crystal X-ray diffraction study. In the IR spectrum, \(\nu(C≡C)\) and \(\nu(CO)\) bands were at 1980 and
1714 cm\(^{-1}\), respectively. The usual NMR features for the Ru(dppe)Cp* groups (Cp* at \(\delta_H\) 1.69, \(\delta_C\) 10.37, 93.60; dppe at \(\delta_H\) 1.99, 3.00; \(\delta_C\) 29.65-30.15; \(\delta_P\) 82.6) were found, the \(^{13}\)C NMR spectrum also having signals for C\(_\beta\) and CO at \(\delta_C\) 120.91 and 158.53, respectively; the resonance for C\(_\alpha\) was not observed, probably being obscured by resonances in the aromatic region. In the ES-MS, ions at \(m/z\) 635, 687 and 1347 are assigned to [Ru(dppe)(C\(_5\)Me\(_5\))]\(^+\), [Ru(CCCO)(dppe)(C\(_5\)Me\(_5\))]\(^+\) and [M + H]\(^+\), respectively.

Scheme 1. Possible mechanism accounting for the synthesis of \{[Cp*(dppe)Ru]C≡C\}_2CO 2 from oxalyl dichloride and NEt\(_3\).

The crystallographic study (Figure 1, Table 1) showed that 2 is comprised of a CO group bearing two -C≡C-Ru(dppe)Cp* moieties, both Cp* ligands being on the same side of the molecule and directed away from the CO group. The Ru-C\(_2\)C(O)C\(_2\)-Ru moiety is essentially planar \((\chi^2 = 695, \delta_{\text{max}} C(2,2') 0.0473 \text{ Å})\). Bond parameters of the Ru(dppe)Cp* group are within the normal ranges [Ru-P 2.2680, 2.2633(6), Ru-C(cp) (av.) 2.251 Å, P-Ru-P 83.21(2), P-Ru-C(1) 78.90, 89.79(7)\(^\circ\)]\(^{36}\). The Ru-C(1) [1.985(2) Å] and C(1)-C(2) distances [1.220(3) Å] are normal for acetylide complexes of the Ru(dppe)Cp* fragment, there being apparently little influence of the CO group on these parameters. Angles at C(1) and C(2) are 174.6(2) and 173.4(3)\(^\circ\),
respectively. For the carbonyl group, C(2)-C(3) and C(3)-O(3) are 1.437(3) and 1.237(5) Å, with angles C(2)-C(3)-C(2') and C(2)-C(3)-O(3) being 116.8(3) and 121.6(2)°.

Figure 1. Plot of a molecule of {[Cp*(dppe)Ru]C≡C}₂CO. Hydrogen atoms omitted for clarity

The chemistry leading to 2 underscores the nucleophilicity of 1, with a proposed route (Scheme 1) involving attack of 1 on ClC(O)C(O)Cl to give an intermediate vinylidene [Ru{=C=CH(C(=O)Cl)}(dppe)Cp*]⁺. This intermediate species was not characterized, but treated with NEt₃ in situ to ultimately give 2, likely through deprotonation of the vinylidene and reaction with a second molecule of 1, followed by loss of HCl and CO. Attempts to synthesise ([Cp(dppe)Ru]C≡C}_₂CO by an analogous route from Ru(C≡CH)(dppe)Cp and oxalyl dichloride afforded only [Ru(=C=CH₂)(dppe)Cp]⁺, identified from its ^1H and ^31P NMR spectra, after work-up. These results confirm earlier observations that Ru(C≡CH)(dppe)Cp is not as strong a nucleophile as 1.
Table 1. Selected bond lengths (Å) and angles (°) for some complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>2</th>
<th>[3]OTf</th>
<th>[5][OTf]₂</th>
<th>6</th>
<th>7</th>
<th>8</th>
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<tr>
<td>Ru(1)-P(1)</td>
<td>2.2680(6)</td>
<td>2.2704(5)</td>
<td>2.315(2)</td>
<td>2.2743(2)</td>
<td>2.282(4)</td>
<td>2.293(2) [P(11)]</td>
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<td>Ru(1)-P(2)</td>
<td>2.2633(6)</td>
<td>2.2829(5)</td>
<td>2.340(1)</td>
<td>2.2702(2)</td>
<td>2.275(3)</td>
<td>2.312(2) [P(12)]</td>
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<td>Ru(2)-P(3)</td>
<td>2.2897(6)</td>
<td>2.302(2)</td>
<td>2.269(3)</td>
<td>2.300(2) [P(21)]</td>
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<tr>
<td>Ru(2)-P(4)</td>
<td>2.3038(5)</td>
<td>2.285(2)</td>
<td>2.256(3)</td>
<td>2.294(2) [P(22)]</td>
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<tr>
<td>Ru(1)-C(cp)</td>
<td>2.231-2.271(2)</td>
<td>2.226-2.275(2)</td>
<td>2.237-2.341(7)</td>
<td>2.2382-2.2754(9)</td>
<td>2.226-2.290(9)</td>
<td>2.255-2.322(6)</td>
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<td>(av.)</td>
<td>2.251</td>
<td>2.255</td>
<td>2.287</td>
<td>2.258</td>
<td>2.262</td>
<td>2.285</td>
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<td>2.248-2.289(2)</td>
<td>2.236-2.291(7)</td>
<td>2.120-2.370(7)</td>
<td>2.243-2.312(6)</td>
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<tr>
<td>(av.)</td>
<td>2.268</td>
<td>2.258</td>
<td>2.240 (disorder)</td>
<td>2.279</td>
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<td>Ru(1)-C(1)</td>
<td>1.985(2)</td>
<td>1.957(2)</td>
<td>1.798(6)</td>
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<td>1.220(3)</td>
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<td>1.236(1)</td>
<td>1.210(12)</td>
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<td>1.437(3)</td>
<td>1.383(3)</td>
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<td>Bond length (Å)</td>
<td>Bond angle (°)</td>
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Bond angles (°):

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<th>Angle (°)</th>
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<tr>
<td>P(2)-Ru(1)-C(1)</td>
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<tr>
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<td>P(3)-Ru(2)-C(5)</td>
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<tr>
<td>P(4)-Ru(2)-C(5)</td>
<td>90.18(6)</td>
</tr>
<tr>
<td>Ru(1)-C(1)-C(2)</td>
<td>174.6(2)</td>
</tr>
<tr>
<td>C(1)-C(2)-C(3)</td>
<td>173.4(3)</td>
</tr>
<tr>
<td>C(2)-C(3)-C(4)</td>
<td>116.8(3)</td>
</tr>
<tr>
<td>C(3)-C(4)-C(5)</td>
<td>173.2(2)</td>
</tr>
<tr>
<td>C(4)-C(5)-Ru(2)</td>
<td>173.8(2)</td>
</tr>
<tr>
<td>C(2)-C(3)-C(4)</td>
<td>121.6(2)</td>
</tr>
<tr>
<td>C(3)-C(4)-C(5)</td>
<td>173.2(2)</td>
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<tr>
<td>C(4)-C(5)-Ru(2)</td>
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<td>C(3)-C(4)-C(5)</td>
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<td>O(3)</td>
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<td>C(3)-O(3)-C(31)</td>
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<tr>
<td>Cp(01)-Ru(1)...Ru(2)-Cp(02)</td>
<td>14.2</td>
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</table>

For 6 (data for one independent molecule): C(5)-O(6) 1.348(1), O(6)-C(7) 1.433(2) Å; C(4)-C(5)-O6 128.7(1), C(5)-O(6)-C(7) 116.2(1)°.
For 7: C(3)-C(31) 1.40(1), C(31)-C(32,33) 1.43(2), 1.42(1) Å; C(2,4)-C(3)-C(31) 119.1(9), 119.9(7), C(3)-C(31)-C(32,33) 121.7, 121.6(9), C(32)-C(31)-C(33) 116.6(9)°.
For 8: C(3)-C(31) 1.382(9), C(31)-C(32,33) 1.444, 1.443(9), C(5)-C(6) 1.376(9), C(6)-C(7) 1.232(8) Å; C(2,4)-C(3)-C(31) 122.9(5), 120.3(5), C(32)-C(31)-C(33) 117.2(6), C(4)-C(5)-C(6) 177.3(7), C(5)-C(6)-C(7) 167.7(7)°.

a Cp(01) and Cp(02) are the centroids of the Cp rings.
Methylation of $\{[\text{Cp}*(\text{dppe})\text{Ru}]\text{C}≡\text{C}\}_2\text{CO}$

The reactions of the bis(metalla-ethynyl)ketone 2 with electrophiles were first examined to establish the relative order of addition to the ketone oxygen and $\text{C}_\beta$ carbon. Addition of one eq. of MeOTf to a solution of 2 in CH$_2$Cl$_2$ resulted in an instantaneous colour change from yellow to deep purple. The single-crystal X-ray structure determination of the product isolated by column chromatography and crystallization showed that methylation has occurred on the carbonyl oxygen $[(\{\text{Ru}(\text{dppe})\text{Cp}^*\})\text{C}_2\text{C}(\text{OME})]\text{OTf}$ [3]OTf (Scheme 2). The site of addition consistent with the Mulliken atomic charges on these atoms in the model system (C, $-0.225$, $-0.228$; O $-0.457$ e) (vide infra). The relatively low frequency $\nu$($\text{C}≡\text{C}$) band (1920 cm$^{-1}$) in [3]OTf is consistent with a degree of allenylidene (Ru=C character in the bridging ligand, as is the presence of a strong band $\nu$(C-O) at 1434 cm$^{-1}$. The $^1$H and $^{13}$C NMR spectra contain resonances for the OMe group at $\delta$C 57.54, while the resonance of $\text{C}_\alpha$ was found at $\delta$C 197.16 ($J_{\text{CP}} = 21$ Hz), also consistent with a significant carbene-like contribution to the molecular structure. Other signals for the Ru(dppe)Cp* moiety are found in the usual regions and single $^{31}$P resonance at $\delta$P 81.2.
Scheme 2. Reactions of \( \{\text{Cp}^*\text{(dppe)}\text{Ru}\}\text{C}≡\text{C}\text{CO} \) with \( \text{MeOTf} \).

In the solid state (Figure 2), the cation \([3]^+\) is not symmetrical, there being different Ru-C separations [Ru(1)-C(1) 1.957(2), Ru(2)-C(5) 1.931(2) Å; the two C(1/5)=C(2/4) [av. 1.241(3) Å] and C(2/4)-C(3) bonds [1.382(3) Å] are not significantly different within each pair. These results are interpreted in terms of contributions from two alkynyl / allenylidene resonance forms, one being favoured perhaps by steric interaction of the OMe group (which is not disordered) with the metal centres within the crystal. The solid state structure represents a frozen configuration which is evidently equilibrating in solution.
Addition of two equivalents of MeOTf to 2 in CH₂Cl₂ gave the same instantaneous colour change to deep purple, indicative of the formation of [3]⁺, which evolved over 3 weeks to give a red solution. The ³¹P NMR of this red solution contained a resonance characteristic of [3]⁺ at δₚ 81.2, together with two pairs of singlets arising from a mixture of minor ([4][OTf]₂: δₚ 81.4, 72.8) and major ([5][OTf]₂: δₚ 80.0, 69.1) products. On heating the mixture to 35 °C, unreacted [3]OTf was consumed to give a solution containing a mixture of [4][OTf]₂ and [5][OTf]₂. However, on attempted separation of the reaction mixture on a silica column, a colour change of the adsorbed material back to purple was observed. Elution (acetone-hexane, 1/1) gave initially [3]OTf (82%) with further elution (acetone / MeOH gradient) affording a small amount (10%) of a red compound [4][OTf]₂. Although [4][OTf]₂ has not been characterized unequivocally, the ES-MS contains the dication of a doubly-methylated complex at m/z 688.190 (calcd 688.178). The IR spectrum also contains ν(C=C=C) and ν(C=C) bands at 1948 and 1538 cm⁻¹, respectively, while the ¹H and ¹³C NMR spectra have resonances which are assigned to =CMe (δ₁H 2.18, δ₁C 29.25) and OMe.
groups ($\delta_H 2.64, \delta_C 58.41$). There are two Ru-C signals at $\delta_C 352.13$ ($J_{CP} = 16$ Hz, vinylidene) and 245.35 ($J_{CP} = 19$ Hz, allenylidene). On the basis of these spectroscopic features, the minor red compound is suggested to be 

\[ \{\text{Cp}^*(\text{dppe})\text{Ru}\}=\text{C}=\text{CHC}(\text{OMe})\text{C}=\text{C}\{\text{Ru}(\text{dppe})\text{Cp}^*}\}[\text{OTf}]_2 \]

([4][OTf]$_2$ (Scheme 2).

The major product ([5][OTf]$_2$) is formed only slowly, but as noted above is rapidly converted to [3]OTf on silica. Purification of [5][OTf]$_2$ proved difficult, but several crystallizations (CH$_2$Cl$_2$ / Et$_2$O) of the crude reaction mixture gave a pure sample. The single-crystal structural determination showed that this complex can be formulated as 

\[ \{\text{Cp}^*(\text{dppe})\text{Ru}\}=\text{C}=\text{CHC}(\text{OMe})=\text{C}=\text{C}\{\text{Ru}(\text{dppe})\text{Cp}^*}\}[\text{OTf}]_2 \]

[5][OTf]$_2$, the protic analogue of [4][OTf]$_2$ (Figure 3). Other spectroscopic data include $\nu$(C=C=C) and $\nu$(C=C) bands at 1960 and 1548 cm$^{-1}$, respectively, and Me ($\delta_H 2.61, \delta_C 58.85$) and vinyl signals ($\delta_H 5.27, \delta_C 148.70$) in the $^1$H and $^{13}$C NMR spectra. The two $^{31}$P resonances described above and which are characteristic of [5]$^{2+}$ attest to the presence of different Ru(dppe)Cp* groups, also indicated by two sets of Cp* resonances at $\delta_H 1.47, 1.57$ and $\delta_C 9.88, 9.98$ and 98.87, 105.24. The formation of [5]$^{2+}$ probably occurs by slow hydrolysis of MeOTf to HOTf during the prolonged reaction time, which then rapidly protonates $C_\beta$ of the C≡C triple bond in [3]$^+$. Indeed, NMR-scale test reactions confirmed the formation of [5]$^{2+}$ following addition of acids to [3]OTf.
While the formal interpretation of the structure of [5]^{2+} is the vinylidene-allenylidene dication shown in Scheme 2, the short Ru-C bonds [Ru(1)-C(1) 1.798(6), Ru(2)-C(5) 1.918(8) Å] suggest a contribution from a carbyne-like structure (cf. Ru≡C 1.766(3) Å in [Ru(≡CCH=CHPh)(dippe)Cp*]^{2+}) (Figure 4).\(^\text{39}\) There is considerable unsaturation in the various C-C bonds [C(1)-C(2) 1.344(9), C(3)-C(4) 1.35(1), C(4)-C(5) 1.25(1) Å], with angles at C(1, 4, 5) being 173.4(5), 169.7(7), 175.2(6)^\text{o}. As expected, bending of the C\(_5\) chain occurs at C(2) and C(3) [124.8, 122.0(6)^\text{o}, respectively].
Figure 4. The vinylidene and carbyne resonance forms of $[5]^{2+}$.

Reaction of 2 with $[\text{NH}_4]\text{PF}_6$ in refluxing MeOH gave low yields of yellow crystalline Ru$\{\text{C}≡\text{CC(O)CH=CH(O\text{Me})}\}(\text{dppe})\text{Cp}^*$ 6 (Scheme 3), the structure being revealed by a single-crystal X-ray determination (Figure 5) and conventional spectroscopic and analytical methods.
Elemental microanalyses, high-resolution ES-MS data and spectroscopic properties agreed with the crystallographically determined structure of \( 6 \). The IR spectrum of \( 6 \) contains \( \nu(C=\equiv C) \) at 2018, \( \nu(C=O) \) at 1621 and \( \nu(C=C) \) at 1556 cm\(^{-1}\). In the NMR spectra, signals at \( \delta_H \) 5.62 and 7.80 [both with \( J_{HH} = 12 \) Hz], \( \delta_C \) 110.85 and 162.39 can be assigned to the trans vinyl group, with the OMe group giving signals at \( \delta_H \) 2.95 and \( \delta_C \) 56.01. The alkynyl C\(_\alpha\), C\(_\beta\) and CO carbon atoms gave \(^{13}\)C NMR resonances at \( \delta_C \) 146.07 (\( J_{CP} = 23 \) Hz), 115.83 and 174.13. In the ES-MS, ions at \( m/z \) 783, 767 and 745 are assigned to \([M + X]^+\) (X = K, Na and H, respectively), their compositions being confirmed by high-resolution measurements.

It seems plausible that the reaction of \( 2 \) in the weakly acidic \([\text{NH}_4]^+ / \text{MeOH}\) medium proceeds via the mechanism outlined in Scheme 3, which has obvious similarities with that proposed in Scheme 2. Initial protonation of the keto-oxygen is followed by methanol attack at C, (attack at C being disfavored by the adjacent oxygen), Fischer
carbene formation and deprotonation. Loss of one Ru(dppe)Cp* group (probably as the solvated cation) occurs by re-protonation.

Scheme 3. The formation of 6 from 2.

Knövenagel condensation
Complex 2 provides an entry point for the preparation of other complexes in which the C₄ chain is interrupted by a functionalized central C atom through derivative chemistry of the carbonyl moiety. The reaction between 2 and malononitrile in the presence of basic alumina occurs much more slowly (3 d) than found in the usual Knövenagel condensation (ca 1 h) (Scheme 4). The product from this reaction forms orange crystals, of which a crystal structure determination showed the expected structure, [{Cp*(dppe)Ru}C≡C]₂C=C(CN)₂ 7. In addition to the usual resonances for the metal-ligand fragments, the ¹³C NMR spectrum contains resonances at δ̂₃ 46.93 [=C(CN)₂], 94.11 (J₁C₃ = 2.2 Hz, C₃), 120.13 (CN) and 165.49 (J₁C₃ = 22 Hz, C₃). The ³¹P NMR contained a broad singlet at δₚ 83.0 for the dppe ligands, likely a
consequence of slower dynamic motion in this relatively sterically congested molecule.

**Scheme 4.** Knövenagel condensation reaction between CH$_2$(CN)$_2$ and 2 to give 7.

Figure 6 shows a plot of a molecule of 7, differences between the two halves being experimentally insignificant. The structure can be formulated as a metallated 1,1-dicyano-2,2-bis(ethynyl)ethene carrying two Ru(dppe)Cp* groups. Bond parameters for the Ru(dppe)Cp* moieties are within the usual ranges and are similar to those found for the ketone 2. Within the C=C(CN)$_2$ group, C(2,4)-C(3) are 1.43, 1.40(1) and C(3)-C(31) is 1.40(1) Å; the angle C(2)-C(3)-C(4) is 121.0(8)°. In the crystal, the two Cp* groups are on the same side of the molecule and opposite to the C(CN)$_2$ group. The cyanocarbon ligand is essentially planar ($\chi^2$ (Ru$_2$C$_6$N$_2$) = 696).

**Figure 6.** Plot of a molecule of (Cp*(dppe)Ru)C≡C$_2$C≡C(CN)$_2$ 7. Only one component of the disordered atoms at Ru(2) has been included (See Experimental).
Of interest here is a similar complex which was obtained from the reaction between \( \text{Ru} \{ \text{C} \equiv \text{CC(N)} = \text{C(N)}_2 \} \{ \text{dppe} \} \text{Cp}^* \), which undergoes ready nucleophilic substitution of the CN group \textit{gem} to the metal centre,\(^{34}\) and the lithiated complex obtained from \( \text{Ru} \{ \text{C} \equiv \text{CC} = \text{CH} \} \{ \text{dppe} \} \text{Cp}^* \) and LiBu (Scheme 5).\(^{38,41}\) The product from this reaction was obtained as a magenta solid and identified spectroscopically and by a single-crystal structure determination (Figure 7) as \( \{ \text{Cp}^*(\text{dppe})\text{Ru} \} \text{C} \equiv \text{CC} \{ = \text{C(N)}_2 \} \text{C} \equiv \text{CC} = \text{C} \{ \text{Ru(dppe)Cp}^* \} \). \(^8\)

\begin{align*}
\text{Scheme 5. Synthesis of } & \{ \text{Cp}^*(\text{dppe})\text{Ru} \} \text{C} \equiv \text{CC} \{ = \text{C(N)}_2 \} \text{C} \equiv \text{CC} = \text{C} \{ \text{Ru(dppe)Cp}^* \} \text{ 8.}
\end{align*}

The IR spectrum of \(^8\) contains a weak \( \nu(\text{CN}) \) band at 2209 \( \text{cm}^{-1} \) and two \( \nu(\text{C}=\text{C}) \) bands at 2111 and 1976 \( \text{cm}^{-1} \), with the latter being broader and more intense. The expected signals for the two similar \( \text{Ru(dppe)Cp}^* \) metal centres are found in the NMR spectra, with two equally intense signals for dppe (\( \delta_p \) 80.8, 81.1) and \( \text{Cp}^* \) ligands (\( \delta_H \) 1.56, 1.64, \( \delta_C \) 10.25, 10.39 and 94.89, 95.84). Despite several attempts a satisfactory elemental microanalysis was not obtained, but high-resolution mass spectrometry of the ions \([M + \text{H}]^+\) and \([M + \text{Na}]^+\) agreed with the calculated formulations.
Figure 7. Plot of a molecule of
\{Cp*(dppe)Ru\}C≡CC\{=C(CN)₂\}C≡CC\{Ru(dppe)Cp*\} 8.

A molecule of 8 is shown in Figure 7, with selected bond parameters collected in Table 1. The two Ru(dppe)Cp* moieties have similar bond lengths and angles within the usual ranges. The two Ru-C bonds are similar at 1.991(6) and 1.975(6) Å, respectively. Within the cyanocarbon ligand, all three C≡C triple bonds have essentially the same bond length, 1.23 Å, with C(sp)-C(sp) and C(sp)-C(sp²) separations C(3)-C(31) 1.376(9) and 1.431(9), 1.418(9) Å, respectively. The ethynyl and diynyl groups are not strictly linear with angles at individual carbon atoms C(1, 2, 5-8) ranging between 167.7(7) and 177.7(5) °. The angles C(2)-C(3)-C(4) and C(32)-C(31)-C(33) are 116.7(6) and 117.2(6)°, respectively, while the dihedral angle between C(33)-C(31)-C(32) and C(2)-C(3)-C(4) about the C(3)-C(31) bond is 5.8(3)°.

UV-vis spectroscopy

The range of colours displayed by complexes 2 - 8 prompted measurement of their UV-vis absorption spectra (Figure 8). The bright yellow parent complex 2 exhibits an
absorption at 387 nm ($\varepsilon$ 24 900 l mol$^{-1}$ cm$^{-1}$) with a shoulder at 339 nm ($\varepsilon$ 15 000 l mol$^{-1}$ cm$^{-1}$) (Figure 7), likely due to a combination of MLCT and intraligand transitions. The substitution of the ketone moiety for the dicyanomethylene in orange-coloured 7 causes a red-shift in these transitions, which appear as a broad transition envelope centered near 477 nm ($\varepsilon$ 30 800 l mol$^{-1}$ cm$^{-1}$), consistent with the MLCT assignment. The increased conjugation pathway offered by the hepta-1,4,7-triyne-3-one-diyl ligand in dark-maroon coloured 8 results in a further red-shift and greater separation of these absorption features leading to two features at 499 ($\varepsilon$ 27 700) and 533 nm ($\varepsilon$ 26 300 l mol$^{-1}$ cm$^{-1}$).

The methylated derivative [3]OTf has a striking purple colour that arises from an intense absorption band at 545 nm ($\varepsilon$ 51 100 l mol$^{-1}$ cm$^{-1}$), consistent with an extensively conjugated ligand backbone or a strong MLCT transition. Methylation to give [4][OTf]$_2$ causes a blue shift in the absorption band, as might be expected from a more localized allenylidene / vinylidene structure, which now appears as a broad, unresolved feature with apparent $\lambda_{\text{max}}$ 489 nm, $\varepsilon$ 32 100 l mol$^{-1}$ cm$^{-1}$. The protonated mono-methylated adduct [5]$^{2+}$ gives a similar spectrum to [4][OTf]$_2$ with a band $\lambda_{\text{max}}$ at 481 nm. However, no molar absorption was recorded as there was partial deprotonation of [5]$^{2+}$ to [3]$^+$, (observed from the appearance of the band at 545 nm) highlighting the acidity of the vinylidene proton.
Figure 8. The UV-vis absorption spectra of 2, [3]OTf, [4][OTf]$_2$, 7 and 8 in CH$_2$Cl$_2$.

**Electrochemistry**

The electrochemical response of bi- and poly-metallic complexes featuring conjugated bridging ligands has been a topic of considerable interest for many years.\textsuperscript{42} It has become clear from these very many investigations that the electronic character of even chemically and structurally similar compounds \{L$_n$M\}(bridge){ML$_n$} can vary dramatically. Consequently, this family of compounds can be used to construct compounds which display: metal-localised redox character, giving rise to well-behaved examples of mixed-valence complexes that may be weakly\textsuperscript{24c,24e,43} or strongly coupled;\textsuperscript{21f} significantly carbon-ligand localized redox-properties and for which mixed-valence descriptions are less appropriate;\textsuperscript{15,44} and a growing range of intermediate situations in which the extensively mixed metal- and carbon-based ligand orbitals\textsuperscript{21e,45} and dynamic conformational effects\textsuperscript{24a} create difficulties in making a clear distinction between the extremes of metal and ligand redox character.
Complex 2 and its derivatives provide a useful opportunity to extend these studies to include an assessment of the influence of a cross-conjugated carbon-rich ligand on the electrochemical response (Table 2) and electronic nature of the complexes and redox-related products, complementing recent investigations with complexes featuring gem-enedithyne and linear polyenediyl based bridging ligands.\textsuperscript{11,15,26}

The closely related complexes 2 and 7 each undergo three sequential one-electron oxidations at moderate potentials, the third being irreversible in each case. The substantial separation of the first two redox processes $E_{1/2}(2) - E_{1/2}(1) = 200 \text{ mV \ (2)}$, $300 \text{ mV \ (7)}$ gives rise to large comproportionation constants $K_C$, indicating the significant thermodynamic stability of the electrochemically generated monocations $[2]^+$ and $[7]^+$.\textsuperscript{46} The electrochemical response of the ‘asymmetric’ complex 8 is essentially identical to that of 7, despite the additional C≡C moiety that has been formally inserted into one ‘arm’ of the bridging ligand. The methylated complex $[3]$OTf displays two oxidation events at significantly more positive potentials than the neutral complexes 2, 7 and 8, no doubt a consequence of the cationic nature of the organometallic fragment. The third oxidation to give $[3]^{4+}$ is likely shifted outside of the accessible solvent window. However, a reduction wave is now also observed at $-1.49 \text{ V}$. Although correlations between optical and electrochemically determined band-gaps need to be made with caution, there is precise agreement between these two measures in the case of $[3]$OTf ($E_{1/2}(1) – E_{1/2}(\text{Red}) = 2.27 \text{ V} \; \lambda_{\text{max}} = 545 \text{ nm} = 2.27 \text{ eV}$).

Unsurprisingly, the dicationic vinylidene derivatives only exhibit one irreversible oxidation wave at even more positive potentials than $E_{1/2}(1)$ in $[3]$OTf, together with an irreversible reduction wave. The cyclic voltammogram of the related mononuclear
complex Ru{C≡CC(CN)=C(CN)\textsubscript{2}}\textsubscript{2}(dppe)Cp* features only a single, irreversible oxidation wave some +420 mV relative to $E_{1/2}$ in 7, indicative of the relative electron-donating and -withdrawing capacities of the Cp*(dppe)RuC≡C– and -CN moieties.

When compared with the most closely related linear polycarbon-bridged bimetallic complexes \{Ru(dppe)Cp*\}_2{\mu-}((C≡C)n) (n = 2, 3, 4) it is readily apparent that the present complexes are oxidized at much less positive potentials than 2 and its derivatives and analogues, and there is a pronounced dependence of $E_{1/2}(2)$–$E_{1/2}(1)$ on the number of alkynyl moieties in the ligand. Spectroelectrochemical and computational studies have shown the substantial contribution from the linear carbon ligand to the redox active orbitals in the polyynediyl family based on ruthenium half-sandwich fragments\textsuperscript{15,44}. Consequently, the radical cations \{Ru(dppe)Cp*\}_2{\mu-}((C≡C)n)\}_+ are arguably better described as metal-stabilised carbon radicals than as true mixed-valence species. However, attempts to investigate many of the complexes described here by spectroelectrochemical methods were hampered by the chemical irreversibility of the redox processes. Therefore, in order to better assess the significance of the electrochemical results, and the ‘mixed-valence’ nature or otherwise of the electrochemically derived products in the cross-conjugated examples, we turned to DFT studies, with computational results correlated with the available spectroscopic data.
Table 2  Electrochemical responses of 2-[5][OTf]$_2$, 7, 8 and related complexes.$^a$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{1/2}(1)^b$</th>
<th>$E_{1/2}(2)$</th>
<th>$\Delta E_{1/2}^c$</th>
<th>$K_e^d$</th>
<th>$E_{1/2}(3)$, $E_{1/2}(4)$</th>
<th>$E_{1/2}$(Red)$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>{Cp*(dppe)Ru*}$^2_2$ &amp; {µ-(C≡C)$<em>2$}$</em>{44b}$</td>
<td>-0.43</td>
<td>+0.22</td>
<td>0.65</td>
<td>1.27 x 10$^{11}$</td>
<td>+1.04</td>
<td>+1.74$^i$</td>
</tr>
<tr>
<td>2</td>
<td>+0.26</td>
<td>+0.46</td>
<td>0.20</td>
<td>2.40 x 10$^3$</td>
<td>+0.84$^i$</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>+0.49</td>
<td>+0.79</td>
<td>0.30</td>
<td>1.17 x 10$^3$</td>
<td>+1.38$^i$</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>+0.48</td>
<td>+0.74</td>
<td>0.26</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru{C≡CC(CN)=C(CN)$<em>2$}(dppe)Cp*$</em>{33b}$</td>
<td>+0.91$^i$</td>
<td></td>
<td></td>
<td></td>
<td>-1.06</td>
<td></td>
</tr>
<tr>
<td>[3]OTf</td>
<td>+0.78</td>
<td>+1.15</td>
<td>0.39$^f$</td>
<td>3.89 x 10$^6$</td>
<td>-1.49$^i$</td>
<td></td>
</tr>
<tr>
<td>[4][OTf]$_2$</td>
<td>+1.12$^i$</td>
<td></td>
<td></td>
<td></td>
<td>-1.03$^i$</td>
<td></td>
</tr>
<tr>
<td>[5][OTf]$_2$</td>
<td>+1.03$^i$</td>
<td></td>
<td></td>
<td></td>
<td>-0.70$^i$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ CH$_2$Cl$_2$ / 0.1 M [Bu$_4$N]PF$_6$ at ca. 25 °C. $^b$ Potentials (V) referenced to [FeCp$_2$/ [FeCp$_2$]$^+$ = +0.46 V or [FeCp*$_2$/ [FeCp*$_2$]$^+$ = -0.02 V.$^{47}$ $^c$ $\Delta E_{1/2} = E_{1/2}(2)-E_{1/2}(1)$. $^d$ $K_e = \exp(\Delta EF /RT)$. $^e$ Half-wave potential of a reduction wave. $^f$ $\Delta E_{1/2}$ was approximated as the separation between the peak potentials of two anodic waves. $^i$ Irreversible, $E_{1/2}$ estimated from peak potentials of an only partially chemically reversible process.

Electronic Structure Calculations

The presence of a cross-conjugated bridging ligand between the Ru(dppe)Cp* fragments in 2, 3, 7 and 8 prompts consideration of the extent of delocalization within the molecular frameworks, and the sensitivity of the distribution of π-electron density to the nature of the C$_\gamma$ substituent.$^{26b}$ Computational models of these complexes ($2'$, $[3']$, 7', 8'), as well as the parent organic gem-diethynylethene ($gem$-DEE) and reference ene-diyne complex 9' (Figure 9), were examined using full ligand sets and
no symmetry restrictions (B3LYP / 3-21G* all atoms). A summary of important bond lengths and angles from the optimized geometries, tables of orbital energies and composition, and plots of key molecular orbitals not otherwise shown are given in the Supporting Information. The gas-phase model geometries generally reproduce the conformations of the metal fragments observed in the crystallographically determined structures which indicate that the conformations adopted in the solid state are strongly influenced by intramolecular steric and electronic factors rather than by crystal packing. The computational models also reproduce individual bond parameters with an approximately 1% over-estimation of bond lengths.

Figure 9. The compounds gem-diethynylethene (gem-DEE) and 9’
The parent gem-diethynylethene (gem-DEE) and derived complex 9′ provide a convenient starting point for discussions and a benchmark for further comparisons with other members of the series. The electronic structures of gem-DEE and substituted derivatives, including bimetallic systems, have been studied at various levels on previous occasions. The in- and out-of-plane π-type orbitals of gem-DEE have been described by Cao and Ren, and a summary of the composition of these π-orbitals together with contour plots are given in the Supporting Information, using the same labeling system as in the previous work. The electronic structure of the Ru(C≡CR)(PR₃)₂Cp′ fragment has also been described in detail on many previous occasions, and it is sufficient to note here that the HOMO and HOMO−1 are approximately orthogonal and essentially derived from out-of-phase mixing of the ethynyl π-system with dₓz and dᵧz metal orbitals (taking z as colinear with the Ru-C≡C σ-bond, y directed at the centroid of the Cp′ ring).

The HOMO of 9′ is derived from the anti-bonding combination of the gem-DEE HOMO (φ₄, out-of-plane ligand π) and in-phase combination of the metal dₓz orbitals, and is therefore delocalized over the 8-atom, cross-conjugated Ru-C≡C-C(=CH₂)-C≡C-Ru chain with substantial contributions from both metal atoms (26%) and the carbon-rich bridge (62%) (Figure 10). The significant weighting of the carbon-rich fragment in the HOMO is common in ruthenium complexes of this type. There is a re-ordering of the HOMO−1 and HOMO−2 orbitals relative to those of the computational model system {trans-Fe(Me)(dHpe)₂}₂(μ-DEE) studied by Cao and Ren, but neither of these orbitals feature any appreciable contribution from the ethenyl π-system. The ligand π* system lies well above the unoccupied orbitals of the Ru(dppe)Cp* fragments and comprises the LUMO+18. Metallation causes a small increase in the C(1)≡C(2) / C(4)≡C(5) and C(3)=CH₂ bond lengths relative to gem-DEE at the same level of theory, in a fashion similar to that noted elsewhere for iron derivatives of gem-DEE.
Perhaps surprisingly, the introduction of the strongly electron withdrawing dicyanomethylene moiety in 7′ has little effect on the composition or order of the occupied orbitals when compared with 9′, although the LUMO is heavily associated with the cyanocarbon π* system (Figure 11). The modest influence of the dicyanomethylene groups on the metal centers is evidenced by the small elongation of the Ru-P bond lengths (Table 4), due to a reduction in metal-phosphine back-bonding. There is also a modest contraction of the Ru(1, 2)-C(1, 5) bonds, likely a consequence of both reduced electrostatic attraction and decreased metal-alkynyl back-bonding. The closely related ynyl-diyl complex 8′ has a pronounced asymmetry in the electronic structure arising from the combination of ethynyl and butadiynyl fragments (Figure 11). Whilst the LUMO is also dominated by the C=C(CN)₂ πₚₚ system, the HOMO and HOMO–1, which are close in energy but not degenerate, are closer in composition to {Cp*(dppe)RuC≡C}⁻ and {Cp*(dppe)RuC≡CC≡C}⁻ fragments, the latter admixed with φ₄. The HOMO-2 and HOMO-3 are derived from in-plane overlaps of the metal and ynyl / diynyl π-systems.
HOMO ($\epsilon = -4.25$ eV)
Ru 15 / C$_2$ 13 / C$_7$ 0 / =O 6 / C$_2$ 20 / Ru 30

LUMO+12 ($\epsilon = 0.07$ eV)
Ru 4 / C$_2$ 11 / C$_7$ 16 / =O 14 / C$_2$ 9 / Ru 4

HOMO ($\epsilon = -6.75$ eV)
Ru 26 / C$_2$ 14 / C$_7$ 0 / =OMe 0 / C$_2$ 11 / Ru 18

LUMO ($\epsilon = -3.83$ eV)
Ru 8 / C$_2$ 19 / C$_7$ 29 / =OMe 8 / C$_2$ 20 / Ru 8

HOMO ($\epsilon = -4.40$ eV)
Ru 13 / C$_2$ 9 / C$_7$ 0 / =C(CN)$_2$ 42 / C$_2$ 9 / Ru 13

LUMO ($\epsilon = -0.99$ eV)
Ru 4 / C$_2$ 14 / C$_7$ 27 / =C(CN)$_2$ 27 / C$_2$ 14 / Ru 4

HOMO ($\epsilon = -4.47$ eV)
Ru 12 / C$_2$ 18 / C$_7$ 0 / =C(CN)$_2$ 0 / C$_2$ 18 / Ru 29

LUMO ($\epsilon = -1.42$ eV)
Ru 3 / C$_2$ 24 / C$_7$ 13 / =C(CN)$_2$ 16 / C$_2$ 12 / Ru 4

HOMO ($\epsilon = -2.76$ eV)
Ru 7 / C$_2$ 17 / C$_7$ 19 / =C(NH)$_2$ 27 / C$_2$ 17 / Ru 7

LUMO+21 ($\epsilon = 1.76$ eV)
Ru 2 / C$_2$ 8 / C$_7$ 6 / =C(NH)$_2$ 31 / C$_2$ 8 / Ru 2
The formal replacement of the methylene =CH₂ moiety in 9' by the ketone =O in 2' has a similar structural effect to that of the dicyanomethylene moieties in 7' and 8' and also causes orbital re-ordering relative to the parent system. The HOMO in 2' lies in the plane of the diethynylketone ligand, and is derived from the *gem-DEE* φ₃ and metal dₓz admixed with the in-plane- oxygen p-type orbital. The HOMO−1 in 2' is similar in composition to the HOMO−1 in 9' whilst the HOMO−2 in 2' lies approximately perpendicular to the plane of the ligand and therefore resembles the HOMO in 9', but with substantially reduced contribution from the C=O moiety. Overall, there is little by way of a fully extended π-conjugated pathway between the metal centers through the diethynylketone-based bridge. The introduction of the ketone moiety has little effect on the relative position of the ligand π* system, which is found in LUMO+12. Methylation of 2' to give [3']⁺ causes the ligand π* system to descend below the level of the unoccupied metal-based orbitals and comprises the LUMO in a fashion similar to that noted for the dicyanomethylene derivatives 7' and 8'. The HOMO of [3']⁺ again features little character from the C, carbon atom and the metal ethynyl fragments are effectively insulated from each other. It would appear that a better description of the intense absorption feature in [3]⁺ is as an MLCT rather than intraligand transition.

To further assess the emerging trend in which strongly electron-withdrawing groups decrease the cross-conjugated π-electron pathway through the 1,1-diethynylethene-derived bridge, the computational model system {Cp*(dppe)RuC≡C{=C(NH₂)₂}Ru(1)≡C(2)-C(3)-C(4)=C(5)-Ru(2)} was constructed (Figure 11). The introduction of the strongly electron-donating NH₂ groups causes a significant increase in the energy cross-conjugated ligand π* system, which is found to comprise the LUMO+21 and LUMO+22 in 10'. However, of more interest is the effect that these substituents have on the composition of the HOMO. The electron-donating groups lead to a substantial increase in the contribution from C, to the HOMO giving rise to a more delocalized π-system along the Ru(1)-C(1)=C(2)-C(3)-C(4)=C(5)-Ru(2) chain. On this basis we would suggest
that more effectively delocalized, cross-conjugated $\pi$-channels can be engineered by introduction of electron-donating groups to the ligand periphery.

**Conclusions**

This work has used the nucleophilic properties of ethynyl compound 1 to generate bis(metalla-ethynyl) ketone 2 from oxalyl dichloride. The electron-withdrawing carbonyl group deactivates the C=C triple bond to metalla-desilylation in attempted syntheses of $\{[\text{Cp'(PP)Ru}]C=C\}_{2}CO$ [$\text{Cp'} = \text{Cp}^*$, $\text{Cp}$; PP = dppe, (PPh$_3$)$_2$] from $(\text{Me}_3\text{SiC}=\text{C})_2\text{CO}$. Methylation of 2 with methyl triflate proceeds initially at the carbonyl oxygen atom rather than the alkynyl C$_\beta$ to give methyl ether [3]OTf. However, a second electrophilic attack (Me$^+$) on [3]$^+$ occurs in a slow reaction at C$_\beta$ to give the bis-methyl adduct [4][OTf]$_2$. Protonation of [3]$^+$ at C$_\beta$ gives vinylidene [5][OTf]$_2$, from which the proton on C$_\beta$ could be readily removed to regenerate [3]$^+$. Upon heating 2 in refluxing MeOH containing [NH$_4$]PF$_6$, partial dissociation of Ru(dppe)Cp$^*$ groups occurred to give the mononuclear complex Ru$_2$C=CC(O)CH=CH(OMe)$_2$(dppe)Cp$^*$ 6. Knövenagel condensation of ketone 2 with CH$_2$(CN)$_2$ gives the dicyanomethylene derivative 7. The related compound $\{\text{Cp'(dppe)Ru}\}C=\text{C}C(\text{CN})_2C=\text{CC}C\{\text{Ru(dppe)Cp}^*\}$ 8 was obtained by nucleophilic displacement of the CN group gem to Ru from Ru$_2$C=CC(CN)=C(CN)$_2$(dppe)Cp$^*$ by LiC=CC=CRu(dppe)Cp$^*$.

Structural studies have shown that the complexes have shorter Ru-C distances than usually found, suggesting that the presence of the CO group in 2 results in major contributions from the vinylidene-allenylidene or carbyne-allenylidene mesomers to the overall structures of these complexes. Electronic structure calculations reveal the $\pi$-electron pathway in 2, [3]$^+$, 7 and 8 is not extensively delocalized through the formally cross-conjugated system. The extent of $\pi$-delocalisation between the metal centres through the cross-conjugated ligand appears to be diminished in response to the introduction of strongly electron-withdrawing groups at C. However, the introduction of additional electron-donating substituents at the 2-position in the metallated ene-1,1-diyne, as in 10, leads to an increase the electron density at C$_\gamma$, with potential for a marked increase in the degree of electronic interaction through these
unusual π-electron systems. Further synthetic efforts in this direction are underway in our laboratories.

**Experimental**

*General comments.* All reactions were carried out under dry nitrogen or argon, although normally no special precautions to exclude air were taken during subsequent work-up. Common solvents were dried, distilled under nitrogen and degassed before use. They were purified as follows: diethyl ether, hexane, and thf were distilled over Na/benzophenone; benzene was distilled from Na; CH$_2$Cl$_2$ and Bu'OH were distilled from CaH$_2$; NEt$_3$ was distilled from KOH; MeOH was distilled from Mg(OMe)$_2$.

Purification of products was carried out either by preparative thin-layer chromatography (TLC) on glass plates (20 x 20 cm$^2$) coated with silica gel (Merck, 0.5 mm thick), flash chromatography on silica gel (Davisil, 40-63 micron), basic alumina (Fluka, Brockmann activity I, pH 10 ± 0.5, 0.05-0.15 mm) or neutral alumina (Fluka, Brockmann activity I, pH 7 ± 0.5, 0.05-0.15 mm).

Elemental analyses were carried out by CMAS, Belmont, Australia, and Campbell Microanalytical Centre, University of Otago, Dunedin, New Zealand.

*Instrumentation.* IR spectra: Bruker IFS28 FT-IR spectrometer. Spectra in CH$_2$Cl$_2$ were obtained using a 0.5 mm path-length solution cell with NaCl windows. Nujol mull spectra were obtained from samples mounted between NaCl discs.

NMR spectra: Varian Gemini 2000 ($^1$H at 300.145 MHz, $^{13}$C at 75.479 MHz, $^{31}$P at 121.501 MHz) or Unity Inova 600 ($^1$H at 599.653 MHz, $^{13}$C at 150.796 MHz) instruments, the latter equipped with a cryo-probe. Samples were contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for $^1$H and $^{13}$C NMR spectra, external H$_3$PO$_4$ for $^{31}$P NMR spectra.

Positive-ion electrospray mass spectra (ES-MS) or high resolution mass spectra (HR-MS) were obtained from samples dissolved in MeOH or MeCN, with added NaOMe as an aid to ionisation when required.$^{51}$ Solutions were injected into Finnigan LCQ (ES-MS, Adelaide), Varian Platform II (ES-MS) or Bruker MicroTOF spectrometers (HR-MS, Waikato) and were calibrated against a standard sodium formate solution.
Nitrogen was used as the drying and nebulising gas. Peaks listed are the most intense of isotopic clusters. UV-vis spectra were obtained with a Varian-Cary 5000 UV-Vis-NIR spectrophotometer. Samples in CH₂Cl₂ were contained in fused quartz cells, path-length 1 cm. Cyclic voltammograms (CVs) were recorded using a PAR Model 263A potentiostat, with a saturated calomel electrode. The cell contained a Pt disk working electrode, and Pt wire counter and pseudo-reference electrodes. Electrochemical samples (1 mM) were dissolved in CH₂Cl₂ containing 0.1 M [NBu₄]PF₆ as the supporting electrolyte. Potentials are given in V vs SCE, with FeCp₂ / [FeCp₂]⁺ (+0.46 V) or FeCp*₂ / [FeCp₂]⁺ (-0.02 V) as internal calibrants.³⁷

**Reagents.** The reagents ClCOCOCl, MeOTf, 2.5 M solution of BuLi in hexanes and NH₄PF₆ were purchased and used as received. The compounds Ru(C≡CH)(dppe)Cp* ¹ ⁴⁴b, Ru{C≡CC(CN)=C(CN)₂}(dppe)Cp* ³ ³ ³ ³ ³ and Ru(C≡CC≡CH)(dppe)Cp* ⁵ ² were prepared by the cited methods.

**Synthesis of {Cp*(dppe)RuC≡C}₂CO ²**
(a) Oxalyl chloride (0.6 ml of a 0.2 M solution in thf, 0.12 mmol) was added to a solution of Ru(C≡CH)(dppe)Cp* (100 mg, 0.15 mmol) in thf (5 ml). The colour of the solution changed rapidly from yellow through red to green. After standing overnight at r.t., NEt₃ (3 ml, excess) was added causing a further colour change to purple. After 1 h, solvent was removed and the residue was taken up in the minimum amount of CH₂Cl₂ (containing 5% NEt₃). The resulting solution was passed through a small column of basic alumina (3.0 x 4.5 cm), eluting with the same solvent mixture. The yellow band was collected and afforded {Cp*(dppe)RuC≡C}₂CO ² (58 mg, 57%) as a yellow solid. Crystals suitable for X-ray diffraction were obtained from hexane. Anal. Calcd (C₇₇H₇₈OP₂Ru₂C₆H₁₄): C, 69.63; H, 6.48; M (solvent free), 1346. Found: C, 69.56; H, 6.61. IR (nujol, cm⁻¹): ν(C≡C) 1980s, ν(C=O) 1714w. ¹H NMR (C₆D₆): δ 1.69 (s, 30H, Cp*), 1.99, 3.00 (2 × m, 4 × CH₂, 2 × dppe), 7.02-7.96 (m, 40H, Ph). ¹³C NMR (C₆D₆): δ 10.37 (s, C₅Me₃), 29.65-30.15 (m, PCH₂CH₂P), 93.60 (s, C₅Me₃), 120.91 (s, C≡), 127.41-139.23 (m, Ph), 158.53 (s, CO). ³¹P NMR (C₆D₆): δ 82.6 (s). ES-MS (MeOH, m/z): 1347, [M + H]⁺; 687, [Cp*(dppe)RuC≡CCO]⁺; 635, [Ru(dppe)Cp*]⁺.
(b) A stirred solution of Ru(C≡CH)(dppe)Cp* (1.0 g, 1.52 mmol) in thf (50 ml) was treated with oxalyl chloride (4.18 ml of 0.2 M solution in thf, 0.834 mmol). The yellow colour initially turned red then rapidly changed to green. After 1 h, the colour was dark bronze. After stirring at r.t. for 2 d, NEt₃ (10 ml) was added to the solution, which became purple. After stirring for one more day, solvent was removed under reduced pressure. The residue was dissolved in a mini amount of CH₂Cl₂ and purified by flash chromatography (silica, 3 x 30 cm; gradient eluted: petroleum spirit-CH₂Cl₂-NEt₃ 40/10/1 to 10/10/1). The first yellow-green band was Ru(C≡CH)(dppe)Cp* (confirmed by ¹H and ³¹P NMR). The second yellow fraction contained crude {Cp*(dppe)RuC≡C}₂CO, which was then passed through another similar column using the same solvent system to give pure 2 as a yellow solid (730 mg, 72%), spectroscopically identical to the sample prepared by the smaller scale route.

Reactions of {Cp*(dppe)RuC≡C}₂CO 2
(a) Methylation. (i) [{Cp*(dppe)RuC≡C}₂C(OMe)]OTf [3]OTf. A solution of {Cp*(dppe)RuC≡C}₂CO (60 mg, 0.045 mmol) in CH₂Cl₂ (10 ml) was treated with MeOTf (5.1 µl, 0.045 mmol) causing the solution colour to instantaneously turn from yellow to purple. The reaction mixture was stirred for 1 h before the solvent was removed under reduced pressure. The residue was purified by flash chromatography (silica, acetone-hexane, 1/1) and the major purple band contained [{Cp*(dppe)RuC≡C}₂C(OMe)]OTf [3]OTf (57 mg, 84%), obtained as a purple solid. X-ray quality crystals were grown from C₆H₆/Et₂O. Anal. Calcd (C₇₉H₈₁F₃O₄P₄Ru₂S): C, 62.86; H, 5.41; M (cation), 1361. Found: C, 62.89; H, 5.34. IR (nujol, cm⁻¹): ν(C≡C) 1920vs; ν(C-O) 1434s; ν(CF/SO) 1267s, 1223s 1185w, 1149m, 1097m, 1069w, 1033m. ¹H NMR (CDCl₃): δ 1.50 (s, 30H, 2 x Cp*), 2.14, 2.49 (2 x CH₂, 2 x dppe), 3.10 (s, 3H, OMe), 7.03-7.46 (m, 40H, Ph). ¹³C NMR (CDCl₃): δ 10.11 (s, C₅Me₅), 29.31-31.11 (m, CH₂P), 57.54 (s, OMe), 96.68 (s, C₅Me₅), 108.25 (s, C≡), 127.93-135.94 (m, Ph), 197.16 [t, JCP = 21 Hz, C]. ³¹P NMR (CDCl₃): δ 81.2 (s). ES-MS (MeOH, m/z): 1361, M⁺; 635, [Ru(dppe)Cp*]⁺.

(ii) (a) [{Cp*(dppe)Ru}C≡CMeC(OMe)=C=C]OTf [OTf]₂ [4]OTf. A solution of {Cp*(dppe)RuC≡C}₂CO (100 mg, 0.074 mmol) in CH₂Cl₂ (10 ml) was
treated with MeOTf (26 µl, 0.230 mmol) in a Schlenk tube under Ar and stirred at 35°C. After 3 weeks, the now red solution was loaded onto a column (acetone-hexane, 1/1), upon which the colour changed to purple. A purple fraction contained [{Cp*(dppe)Ru}=C=CHC(OMe)=C=C={Ru(dppe)Cp*}]OTf [3]OTf (92 mg, 82%). A red band was eluted with acetone and MeOH, then NaCl (10-50 mg) was then added to the top of the column to increase the ionic strength of the eluent to give

[4] [{Cp*(dppe)Ru}=C=CHC(OMe)=C=C={Ru(dppe)Cp*}]OTf as a dark red solid (13 mg, 10%). Anal. Calcd (C₈₈H₇₁F₅O₅P₃Ru₂S₂): C, 58.13; H, 5.06; M (cation), 1376. Found: C, 57.61; H, 5.16. IR (nujol, cm⁻¹): ν(Ru=C=C=) 1948s, ν(C=C) 1538s, ν(CF) 98.77, 104.73 (2 × 1376 w, CF = 16 Hz, Ru=C=CMe). ¹H NMR (CDCl₃): δ 1.53, 1.63 (2 × s, 2 × 15H, 2 × Cp*), 2.18 (s, 3H, =CMe), 2.60, 2.85 (2 × m, 4 × CH₂, 2 × dppe), 2.64 (s, 3H, OMe), 6.94-7.66 (m, 40H, Ph). ¹³C NMR (CDCl₃): δ 9.94, 10.21 (s, 2 × C₅Me₂), 29.25 (s, =CMe), 29.10-30.06 (m, 2 × CH₃P), 58.41 (s, OMe), 58.85 (s, OMe), 72.8 (m, OMe). m/z CP⁺: 688.190 (688.178).

(iii) [{Cp*(dppe)Ru} =C=CHC(OMe)=C=C={Ru(dppe)Cp*}]OTf [5]OTf. A solution of {Cp*(dppe)Ru=C=C=CO} (80 mg, 0.060 mmol) in CH₂Cl₂ (10 ml) was treated with MeOTf (14 µl, 0.122 mmol) under Ar. The solution turned purple straight away and after 3 weeks was red. Et₂O was layered onto the solution to induce crystallisation, and the resulting solid was similarly recrystallised to give

[5] [{Cp*(dppe)Ru} =C=CHC(OMe)=C=C={Ru(dppe)Cp*}]OTf [5]OTf (60 mg, 60%) as dark red crystals. X-ray quality crystals were grown from CH₂Cl₂/Et₂O. Anal. Calcd (C₈₈H₇₁F₅O₅P₃Ru₂S₂): C, 57.90; H, 4.98; M (cation), 1362. Found: C, 56.98; H, 5.05. IR (nujol, cm⁻¹): ν(C=C=C) 1960m, ν(C=C) 1548m, ν(CF/Me) 1272m, 1221w, 1152m, 1097w, 1031m. ¹H NMR (CDCl₃): δ 1.47, 1.57 (2 × s, 2 × 15H, 2 × Cp*), 2.45, 2.96 (2 × m, 4 × CH₂, 2 × dppe), 2.61 (s, 3H, OMe), 5.27 (s, 1H, =CH) 7.00-7.54 (m, 40H, Ph). ¹³C NMR (CDCl₃): δ 9.88, 9.98 (2 × s, 2 × C₅Me₂), 27.52-27.83, 29.37-29.68 (2 × m, 2 × CH₃P), 58.85 (s, OMe), 98.87, 105.24 (2 × s, 2 × C₅Me₂), 116.02, 137.93 (2 × s, C), 120.97 [q, J_CF = 321 Hz, CF₃], 128.04-134.42 (m, Ph), 148.70 (s, =CH), 242.54 [t, J_Cp = 20 Hz, Ru=C=C=C], 344.44 [t, J_CF = 16
Hz. Ru=CN]. \(^{31}\)P NMR (CDCl\(_3\)): \(\delta\) 80.0 (s), 69.1 (s). ES-MS (MeCN, \(m/z\)): 1361, [{\(\text{Cp*(dppe)RuC=Cl}_2\text{C(OMe)}\})\(^+\)]. HR-MS (MeCN, \(m/z\)): Found (calcd): 1361.319 (1361.332), [{\(\text{Cp*(dppe)RuC=Cl}_2\text{C(OMe)}\})\(^+\)].

(b) *Protonation. Preparation of Ru\{C=CC(O)CH=CH(OMe)\} \((dppe)\text{Cp}* \text{6}.* MeOH (7 ml) was added to a mixture of [{\(\text{Cp*(dppe)RuC=Cl}_2\text{C} \text{CO}\} \text{40 mg, 0.03 mmol}] and [\(\text{NH}_4\text{PF}_6\) (10 mg, 0.06 mmol) and the mixture was heated under reflux for 7 h. After removal of solvent, the residue was dissolved in acetone and purified by preparative t.l.c. (acetone/hexane, 1/2). The major yellow band (\(R_t = 0.47\)) contained Ru\{C=CC(O)CH=CH(OMe)\} \((dppe)\text{Cp}* \text{6} (13 mg, 6\%)\), obtained as yellow crystals (C\(_8\)H\(_6\) / hexane). Anal. Calcd (C\(_{24}\)H\(_{44}\)O\(_2\)P\(_2\)Ru): C, 67.82; H, 5.96; M, 744. Found: C, 68.01; H, 6.18. IR (CH\(_2\)Cl\(_2\), cm\(^{-1}\)): \(\nu(C=\equiv)\) 2018s, \(\nu(C=\equiv)\) 1621m, \(\nu(C=\equiv)\) 1556m (br). \(^1\)H NMR (C\(_6\)D\(_6\)): \(\delta\) 1.56 (s, 15H, \(\text{Cp*}\)), 1.84, 2.71 (2 x m, 4H, dppe), 2.95 (s, 3H, OMe), 5.62 [d, \(J_{HH} = 12\) Hz, 1H, H\(_1\)], 7.80 [d, \(J_{HH} = 12\) Hz, 1H, H\(_2\)], 6.98-7.86 (m, 20H, Ph). \(^{13}\)C NMR (C\(_6\)D\(_6\)): \(\delta\) 10.27 (s, \(\text{C}_5\text{Me}_3\)), 29.53 (m, CH\(_2\)), 56.01 (OMe), 93.60 (\(\text{C}_5\text{Me}_3\)), 110.85 (s, C\(_1\)), 115.83 (s, C\(_6\)), 127.84-138.89 (Ph), 146.07 [t, \(J_{(CP)} = 23\) Hz, C\(_4\)], 162.39 (C\(_6\)), 174.13 (C=O). \(^{31}\)P NMR (C\(_6\)D\(_6\)): \(\delta\) 80.9 (s). ES-MS (MeOH + NaOMe, \(m/z\)): 783.161 (calcd 783.150), \([M + K]^+\); 767.186 (767.176), \([M + Na]^+\); 745.205 (745.194), \([M + H]^+\).

(c) *Knövenagel condensation.* To a mixture of [{\(\text{Cp*(dppe)RuC=Cl}_2\text{C} \text{CO}\} \text{89 mg, 0.066 mmol}] and basic \(\text{Al}_2\text{O}_3\) (80 mg) was added CH\(_2\)Cl\(_2\) (8 ml) and reaction mixture was heated at reflux for 3 d, the colour turning from yellow to orange. Solvent was removed and the residue was purified by preparative t.l.c. (acetone-hexane, 3/7) to give a red-orange solid (\(R_t = 0.56\)), which afforded [{\(\text{Cp*(dppe)RuC=Cl}_2\text{C} = \text{C(CN)}_2\} \text{7 (27 mg, 29\%) as an orange solid. X-ray quality crystals were grown from CH\(_2\)Cl\(_2\)/hexane]. Anal. Calcd (C\(_{66}\)H\(_{85}\)N\(_3\)P\(_2\)Ru\(_2\)): C, 68.95; H, 5.64; N, 2.01; M, 1394. Found: C, 69.10; H, 5.89; N, 2.04. IR (CH\(_2\)Cl\(_2\), cm\(^{-1}\)): \(\nu(C=\equiv)\) 2199w, \(\nu(C=\equiv)\) 1967vs, \(\nu(C=\equiv)\) 1481w, 1435w, 1399w, 1303w. (nujol): \(\nu(C=\equiv)\) 2193m, \(\nu(C=\equiv)\) 1995s, 1971vs, \(\nu(C=\equiv)\) 1435s, 1401m, 1301m. \(^1\)H NMR (C\(_6\)D\(_6\)): \(\delta\) 1.63 (s, 30H, 2 x \(\text{Cp*}\)), 2.39 (m, 4 x CH\(_2\)), 2 x dppe), 7.04-7.31, 7.74 (2 x m, 40H, Ph). \(^{13}\)C NMR (C\(_6\)D\(_6\)): \(\delta\) 10.76 (s, \(\text{C}_5\text{Me}_3\)), 30.40 (m, CH\(_2\))P, 46.93 [s, \(\text{C(CN)}_2\)], 94.11 [t, \(J_{CP} = 2.2\) Hz, Ru-C=\(\equiv\)], 94.85 (s, \(\text{C}_5\text{Me}_3\)), 120.13 (s, CN), 127.91-139.86 (m,
Preparation of \{Cp*(dppe)Ru\}C≡C\{C≡C(CN)\}_2\}C≡CC\{Ru(dppe)Cp*\}^8

A solution of Ru(C≡CC≡CH)(dppe)Cp* (74 mg, 0.108 mmol) in thf (20 ml) was cooled to -78˚C and treated with BuLi (0.047 ml of 2.5 M solution in hexane, 0.118 mmol). After 30 min Ru\{C≡CC≡C(CN)\}_2\}C≡CC\{Ru(dppe)Cp*\} (75 mg, 0.098 mmol) was added to the solution. The mixture was allowed to warm to r.t. and after 90 min was reddish purple. The solvent was removed and the residue was dissolved in the minimum amount of toluene and loaded onto a column (flash silica, acetone-petroleum spirit, 1/4). The magenta band was collected and afforded \{Cp*(dppe)Ru\}C≡C\{C≡C(CN)\}_2\}C≡CC\{Ru(dppe)Cp*\}^8 as a dark magenta solid (28 mg, 20%). X-ray quality crystals were grown from C₆D₆ / MeOH. IR (CH₂Cl₂, cm⁻¹): ν (C≡N) 2209w, ν(C≡C) 2111s, 1994vs, ν(C=C) 1435m, 1419m. ¹H NMR (C₆D₆): δ 1.56, 1.64 (2 x s, 15H, Cp*), 2.43, 2.90 (2 x m, 4 x CH₂, 2 x dppe), 7.04-7.83 (m, 40H, Ph). ¹³C NMR (CD₂Cl₂): δ 10.25, 10.39 (2 x s, C₅Me₅), 29.50-30.25 (m, CH₂P), 72.78, 94.69, 95.70, 100.27, 125.88, 138.45 (6 x s, C), 94.89, 95.84 (2 x s, C₅Me₅), 118.99, 119.12 (2 x s, CN), 128.20-137.95 (m, Ph), 162.57, 188.35 [2 x t, J_Cp = 23, 23 Hz, C. (RuC₄), C.‘ (RuC₂), respectively]. ³¹P NMR (C₆D₆): δ 81.1 (s), 80.8 (s). ES-MS (MeOH, m/z): 1441, [M + Na]⁺; 1418, M⁺; 676, [Ru(NCMe)(dppe)Cp*]⁺; 635, [Ru(dppe)Cp*]⁺. HR-MS: Found (calcd): [M + Na]⁺, 1441.328 (1441.310); [M + H]⁺, 1419.319 (1419.328). Satisfactory elemental analyses could not be obtained.

Structure determinations

Diffraction data were measured using either an Oxford Diffraction Xcalibur or Gemini diffractometer at 100K (150K for 7) with Mo-Kα radiation, λ = 0.71073 Å (Cu-Kα, λ = 1.54178 Å for [5][OTf]₂, 7). Following multi-scan or analytical absorption corrections and solution by direct methods, the structures were refined using full matrix least squares refinements on F² using the SHELXL 97 program. Except where stated below, anisotropic displacement parameter forms were refined for the non-hydrogen atoms; hydrogen atoms were treated as a riding model.
Pertinent results are given in Figs. 1-7 (which show non-hydrogen atoms with 50% probability amplitude displacement ellipsoids (20% for 7, 30% for 5, 9) with hydrogen atoms removed for clarity) and in Tables 1 and the supporting information.

**Compound [3]OTf:** One phenyl ring and two of the solvent benzene molecules are each disordered over two sites. The site occupancies of these were refined with the same value on the basis of contact distances and after trial refinement showed no significant differences between the individual parameters. The occupancies of the major and minor components refined to 0.607(3) and 1-0.607(3). The geometries of the disordered solvent molecules were restrained to ideal values.

**Compound 7:** Five phenyl rings and the Cp* ligand on Ru(2) are disordered over two sets of sites, with occupancy factors set at 0.5 after trial refinement. Electron density due to a solvent molecule was modelled as a dichloromethane molecule disordered about a crystallographic 2-fold axis, the overall site occupancy being constrained to 0.5 after trial refinement. The geometries of the disordered phenyl and Cp* rings and of the solvent were restrained to ideal values. The carbon atoms of the disordered Ph rings were refined with isotropic displacement parameters.

**Computational details**

All DFT computations were carried out with the Gaussian 03 package. The model geometries were optimised at the B3LYP/3-21G* level of theory, to reduce computational effort, with no symmetry constraints, in a manner similar to that reported elsewhere. MOs and frequencies were computed on these optimised geometries at the same level of theory. All geometries were identified as minima (no imaginary frequencies). A scaling factor of 0.95 was applied to the calculated frequencies. The MO contributions were generated using the GaussSum package and plotted using GaussView 5.0.
Supporting Information

Tables of crystallographic refinement details. Tables of optimized geometries, orbital energies and composition from \textit{gem-DEE}, 2’, 3’, 7’, 8’, 9’ and 10’. Plots of key orbitals of \textit{gem-DEE} and 9’. CIF files, figures and tables giving all crystallographic data and selected bond distances. This material is available free of charge via the Internet at \url{http://pubs.org.acs}. Full details of the structure determinations (except structure factors) have also been deposited with the Cambridge Crystallographic Data Centre as CCDC 897230 [2], 897232 [3]OTf, 897234 [5][OTf]$_2$, 897235 [6], 897236 [7], 897237 [8]. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: \url{http://www.ccdc.cam.ac.uk}).

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Notes

The authors declare no competing financial interest.

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