

Further chemistry of ruthenium butatrienylidene complexes

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Abstract

Several complexes have been obtained from reactions carried out in early attempts to prepare the diyne complexes $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CR})(\text{dppe})\text{Cp}^*$ ($\text{R} = \text{H}, \text{SiMe}_3$). These have been identified crystallographically as the acyl complex $\text{Ru}\{\text{C}\equiv\text{CC}(\text{O})\text{Me}\}(\text{dppe})\text{Cp}^*$ (**3**), the cationic imido complex $[\text{Ru}\{\text{C}\equiv\text{CC}(\text{=NH}_2)\text{Me}\}(\text{dppe})\text{Cp}^*]\text{PF}_6$ (**4**), the binuclear butenyneallenylydene $[\{\text{Ru}(\text{dppe})\text{Cp}^*\}_2\{\mu\text{-C}\equiv\text{CC}(\text{OMe})\text{=CHCMe}=\text{C}=\text{C}=\text{C}\}]\text{PF}_6$ (**5**), and the bis(ethynyl)cyclobutenylidene $[\{\text{Ru}(\text{dppe})\text{Cp}^*\}_2\{\mu\text{-C}\equiv\text{CC}_4\text{H}_2(\text{SiMe}_3)\text{C}\equiv\text{C}\}]\text{PF}_6$ (**6**). NMR studies of **5** have revealed the existence of two isomers. Plausible routes for their formation from the putative butatrienylidene intermediate $[\text{Ru}(\text{=C}=\text{C}=\text{C}=\text{CH}_2)(\text{dppe})\text{Cp}^*]^+$ (**A**) are discussed.

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1. Introduction

The chemistry of metal σ -alkynyl complexes and their conjugate acids, the corresponding vinylidenes, continues to provide novel routes into a wide variety of organic systems [1]. The higher unsaturated carbenes, such as allenylidenes, have also been developed to the point where useful syntheses of metal-free molecules can be achieved [2]. Not so well explored are the butatrienylidenes, which have been largely characterised on the basis of their chemical reactions, the solid complexes proving difficult to isolate [3]. Ruthenium carbonyl cluster-stabilised examples of this ligand have been described some years ago [4] and the first structurally characterised mononuclear example was the iridium complex *trans*- $\text{IrCl}(\text{=C}=\text{C}=\text{C}=\text{CPh}_2)(\text{PPr}_3^f)_2$ [5]. The unusual metal-substituted derivative, $[\text{Fe}\{\text{=C}=\text{C}=\text{C}=\text{CH}[\text{Fp}^*(\text{dppe})\text{Cp}^*]\}(\text{CO})_2\text{Cp}^*]\text{PF}_6$, has been described by Lapinte and coworkers [6].

Several groups have reported reactions which can be rationalised as proceeding via butatrienylidene intermediates, formed in situ from reactions of 1,3-diynes with electron-rich metal complexes containing labile ligands. Most chemistry has been generated from *trans*- $[\text{RuCl}(\text{=C}=\text{C}=\text{C}=\text{CH}_2)(\text{dppm})_2]^+$ [7] and $[\text{Ru}(\text{=C}=\text{C}=\text{CH}_2)(\text{PPh}_3)_2\text{Cp}]^+$ [8] (from $\text{HC}\equiv\text{CC}\equiv\text{CH}$ and *cis*- $\text{RuCl}_2(\text{dppm})_2$ or $[\text{Ru}(\text{thf})(\text{PPh}_3)_2\text{Cp}]^+$, respectively). This paper describes further chemistry which is considered to arise from complexes analogous to the latter but which, as in the earlier examples, have not been isolated.

2. Results

2.1. Synthesis and characterisation of ruthenium complexes with C_4 chains

2.1.1. $\text{Ru}\{\text{C}\equiv\text{CC}(\text{O})\text{Me}\}(\text{dppe})\text{Cp}^*$ (**3**)

When the chloro-ruthenium complex $\text{RuCl}(\text{dppe})\text{Cp}^*$ (**1**) was treated with an excess of $\text{LiC}\equiv\text{CC}\equiv\text{CSiMe}_3$ at -78°C , in an attempt to synthesise $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{dppe})\text{Cp}^*$ (**2**), the only product was the hydride $\text{RuH}(\text{dppe})\text{Cp}^*$. No evidence for the formation of **2** was

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obtained. This result is in contrast to the analogous reaction between $\text{RuCl}(\text{CO})_2\text{Cp}$ and $\text{LiC}\equiv\text{CC}\equiv\text{CSiMe}_3$, which gave $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{CO})_2\text{Cp}$ in a reasonable yield (72%) [10]. This suggests that the carbonyl-containing chloro complex is more susceptible to nucleophilic attack than the much more electron-rich **1**. The increased steric hindrance imposed by the bulky phosphine and Cp^* ligands, relative to the smaller carbonyl and Cp ligands, would also hinder nucleophilic attack.

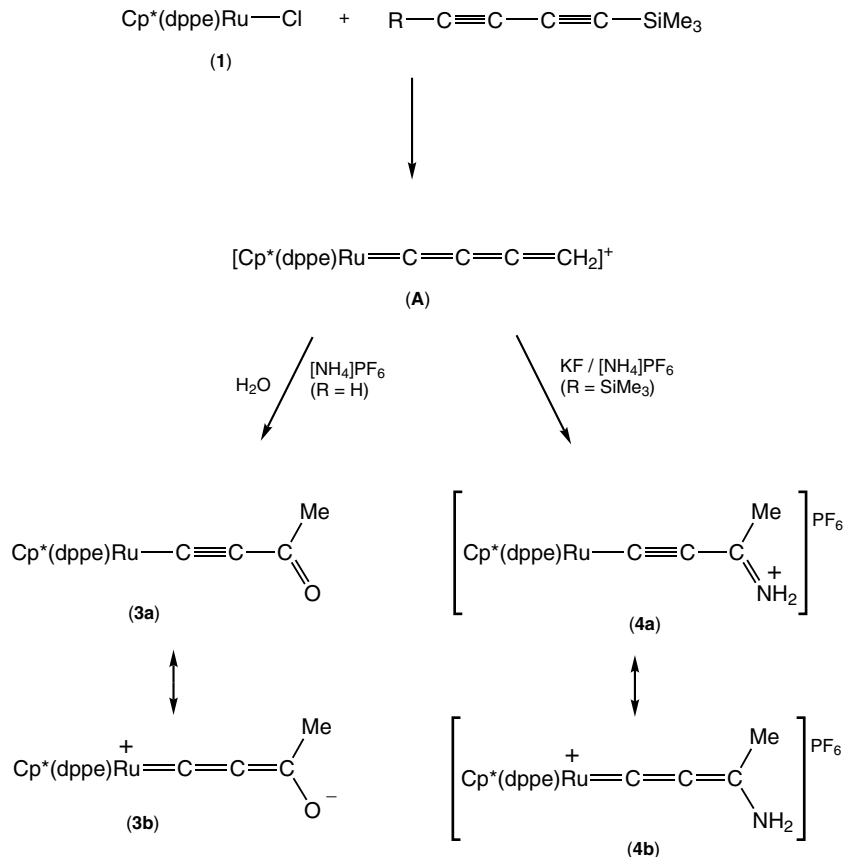
The reaction of **1** with an excess of $\text{HC}\equiv\text{CC}\equiv\text{CSiMe}_3$ in the presence of $[\text{NH}_4]\text{PF}_6$ in MeOH resulted in the initial orange suspension quickly changing to a green solution. Work-up using a basic alumina column gave bright yellow $\text{Ru}\{\text{C}\equiv\text{CC}(\text{O})\text{Me}\}(\text{dppe})\text{Cp}^*$ (**3**; Scheme 1) together with an intense blue fraction, discussed below. Characterisation of **3** was initially from the single-crystal structure determination (see below) and spectroscopic data [two $\nu(\text{CC})$ bands at 2024 and 2006, $\nu(\text{CO})$ at 1605 cm^{-1} , resonances for Cp^* and Me at δ_{H} 1.59 and 1.89, and δ_{C} 9.78, 32.37 and 93.71] also being consistent with this formulation. The $\nu(\text{CC})$ frequencies are lower than those found in the related complex $\text{Ru}\{\text{C}\equiv\text{CC}(\text{O})\text{Me}\}(\text{PPh}_3)_2\text{Cp}$ ($2048, 2011\text{ cm}^{-1}$) [11] as a result of the enhanced electron donating abilities of the Cp^* and dppe ligands in **3**. In the ^{13}C NMR spectrum, signals for C(1) and C(2)

are found at δ 159.24 (t) and 118.88(s). These data are consistent with some stabilisation of resonance form **3b** by increased back-bonding into the allenylidene ligand, although the upfield position of these resonances suggests that resonance structure **3a** is the major contributor to the overall structure.

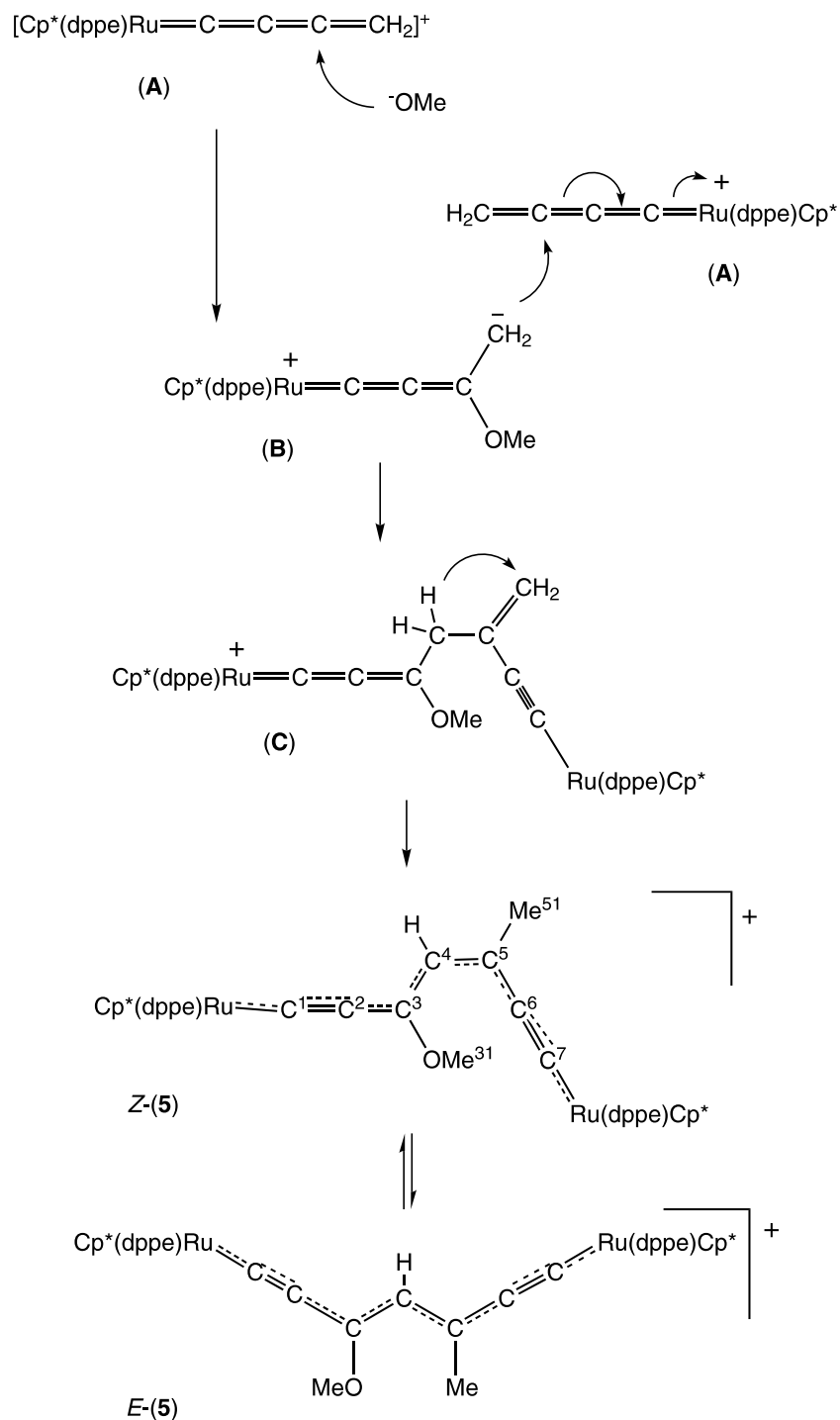
2.1.2. $[\text{Ru}\{\text{C}\equiv\text{CC}(\text{=NH}_2)\text{Me}\}(\text{dppe})\text{Cp}^*]\text{PF}_6$ (**4**)

It was anticipated that the reaction of **1** with an excess of $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$ in the presence of KF and $[\text{NH}_4]\text{PF}_6$ in MeOH solution might give $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})\text{Cp}^*$. In this reaction, $[\text{NH}_4]\text{PF}_6$ was added to assist the dissociation of the Ru–Cl bond, while KF was used both as a desilylating agent and a source of base to ensure the deprotonation of the expected butatrienylidene intermediate **A**. The reaction has been used with some success in earlier syntheses of related alkynyl- and diynyl-ruthenium complexes [12]. As the reaction proceeded, the colour quickly changed from the initial orange to a deep blue and then gradually lightened to green. Work-up by preparative t.l.c. gave, as the major product, an orange complex identified crystallographically as $[\text{Ru}\{\text{C}\equiv\text{CC}(\text{=NH}_2)\text{Me}\}(\text{dppe})\text{Cp}^*]\text{PF}_6$ (**4**; Scheme 1).

The IR spectrum of **4** contains two bands at 1982 and 1651 cm^{-1} that were assigned to $\nu(\text{CC})$ and $\nu(\text{C}=\text{N})$,



Scheme 1.



Scheme 2.

respectively, together with $\nu(\text{NH})$ bands between 3271 and 3449 cm^{-1} . In addition to the usual resonances, the ^{13}C NMR of **4** contains a triplet at δ 216.37 [$J(\text{CP})$ 20 Hz], which is significantly downfield from the usual value of δ ca 120 found for $\text{Ru}-\text{C}\equiv$ in related alkyne-ruthenium complexes. Singlet resonances at δ 121.72 and 156.74 are assigned to C(2) and C(3), respectively, by comparison with related complexes [13].

Two interconverting resonance forms can describe the structure of **4**, as illustrated in Scheme 1. The relative contributions of the alkyne **4a** and allenylidene **4b** forms in related complexes have been shown to depend on the nature of the heteroatom and its ability to stabilise the positive charge [13,14]. Generally, when the heteroatom is nitrogen, there are strong contributions from resonance structure **4a**. However, in the case of complex

4, allenylidene form **4b** would be stabilised by the electron-rich Ru(dppe)Cp* fragment, due to increased back-bonding into the allenylidene ligand [13]. The spectroscopic and structural data (below) suggest that the structure of **4** lies between these two extremes. The observation of a $\nu(\text{C}=\text{N})$ band in the IR spectrum together with the X-ray data which establish bond lengths close to the values expected for Ru–C single and C \equiv C triple bonds support the alkynyl form **4a**. However, a contribution from the allenylidene form **4b** can be seen in the ^{13}C NMR spectrum, with resonances for the C₁ and C₂ atoms shifted significantly downfield with respect to those found in Ru(C \equiv CH)(dppe)Cp* [δ 120.58 (C₁), 92.99 (C₂)] [9b].

2.2. Isolation and characterisation of ruthenium complexes with C₇ chains

2.2.1. [$\{\text{Cp}^*(\text{dppe})\text{Ru}\}\text{C}\equiv\text{CC}(\text{OMe})=\text{CHCMe}=\text{C}=\text{C}=\{\text{Ru}(\text{dppe})\text{Cp}^*\}$] PF_6 (**5**)

A feature of both the reactions described above is the formation of intensely coloured blue products. That accompanying **3** could be isolated using column chromatography (alumina), eluting with Et₂O/acetone mixtures. An analytically pure sample was obtained after a second chromatography and crystallisation (acetone–hexane). The compound was identified as the cationic binuclear product [$\{\text{Cp}^*(\text{dppe})\text{Ru}\}\text{C}\equiv\text{CC}(\text{OMe})=\text{CHCMe}=\text{C}=\text{C}=\{\text{Ru}(\text{dppe})\text{Cp}^*\}$] PF_6 (**5**; Scheme 2) by a single-crystal X-ray structure determination coupled with a detailed NMR study, which included HSQC and HSBC experiments. The latter showed that an equilibrium mixture of the *E* and *Z* isomers are present, resulting from restricted rotation around the C(4)–C(5) bond. Attempts to separate the isomers by t.l.c. were not successful. While no changes in the relative ratios were detected at low temperature (–80 °C), coalescence of the two resonances for the proton attached to C₄ occurs on heating the sample above 55 °C.

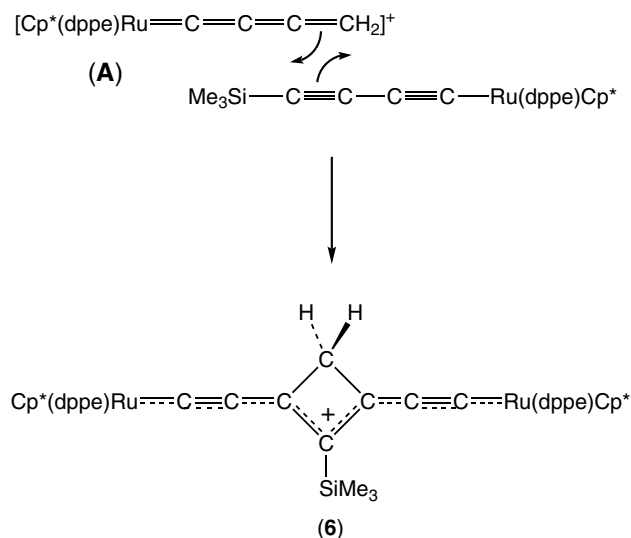
The NMR spectra of **5**, including 2D HSQC and HMBC NMR experiments, are consistent with the X-ray structure and support the presence of the H, OMe and Me pendant groups on the C₇ bridging ligand. Additionally, many of the resonances occur as pairs of signals with constant relative intensities of 56/44 which, as described below, are ascribed to *E* and *Z* isomers, respectively [with respect to the C(4)=C(5) bond]. Thus, in the ^1H NMR spectrum, two distinct ^1H resonances were found for the Cp* resonances (between δ 1.58 and 1.62) and also for the =CH (δ 5.44/5.14), OMe (δ 3.24/2.87) and Me groups (δ 1.69, 1.47) attached to the bridging ligand. The ^{13}C NMR spectrum similarly contained pairs of signals at δ 10.18/10.14 (C₅Me₅; only one singlet found for each isomer), 97.04/96.84 and 96.31/96.21 (C₅Me₅), 58.03/58.11 (OMe) and δ 26.17/31.81 (CMe). Signals for various atoms in the substituted C₇

chain were assigned to atoms C(2) (δ 125.78/126/40), C(3) (155.50/154.83), C(5) (122.42/119.56), C(6) (142.55/141.61) and C(8) (150.21/146.28) using the HSQC and HSBC experiments. All pairs have the same 56/44 relative intensities. We were not able to assign definitively the resonances for the Ru-bonded carbons C(1,7), for which four resonances in the region δ 203.4–209.76 were observed. The chemical shifts of these resonances lie between the characteristic vinylidene Ru=C (δ ca. 340.0) and alkynyl Ru–C \equiv (δ ca. 120.0) carbon resonances. The ^{31}P NMR spectrum contained two sets of signals for the dppe ligands (δ 81.10 and 80.83/81.29 and 80.41) together with a single septet at δ –143.38 ([PF₆][–]).

Evidence for the stereochemical assignments is found in the 2D ROESY NMR spectrum that confirmed the minor isomer had the *Z* configuration around C(4)–C(5) with a ROESY interaction observed between the proton directly attached to atom C(4) and the methyl protons attached to C(51) (crystallographic numbering). No such interaction was observed with the major isomer, suggesting it has the *E* configuration. HSQC 2D NMR confirmed that resonances at δ 122.42, 58.03 and 26.17 found in the ^{13}C NMR spectrum of the *E* isomer were due to C(4), C(31) and C(51), respectively, with cross peaks being observed between the ^1H and ^{13}C resonances. Other resonances were assigned upon the basis of long-range HMBC 2D NMR experiments.

2.2.2. [$\{\text{Ru}(\text{dppe})\text{Cp}^*\}_2\{\mu\text{-C}\equiv\text{CC}_4\text{H}_2\text{(SiMe}_3\text{)C}\equiv\text{C}\}$] PF_6 (**6**)

A second deep blue product was isolated from the reaction which afforded **3** and **5**. Only formed in trace quantities, it was first obtained whilst attempting to crystallise a crude sample of **5** from CH₂Cl₂/hexane.



Scheme 3.

Several block-like crystals were identified from the X-ray structural study as the cyclobutenylidene complex $[\{\text{Ru}(\text{dppe})\text{Cp}^*\}_2\{\mu\text{-C}\equiv\text{CC}_4\text{H}_2(\text{SiMe}_3)\text{C}\equiv\text{C}\}]\text{PF}_6$ (**6**; Scheme 3), a formulation supported by an ion in the

ES-MS at m/z 1440. A crude sample of **5** contained ions corresponding to M^+ at m/z 1401 (**5**) and at m/z 1440 (**6**). MS-MS of the ion centred at m/z 1440 did not result in fragmentation to give m/z 1401. Unfortunately, we have

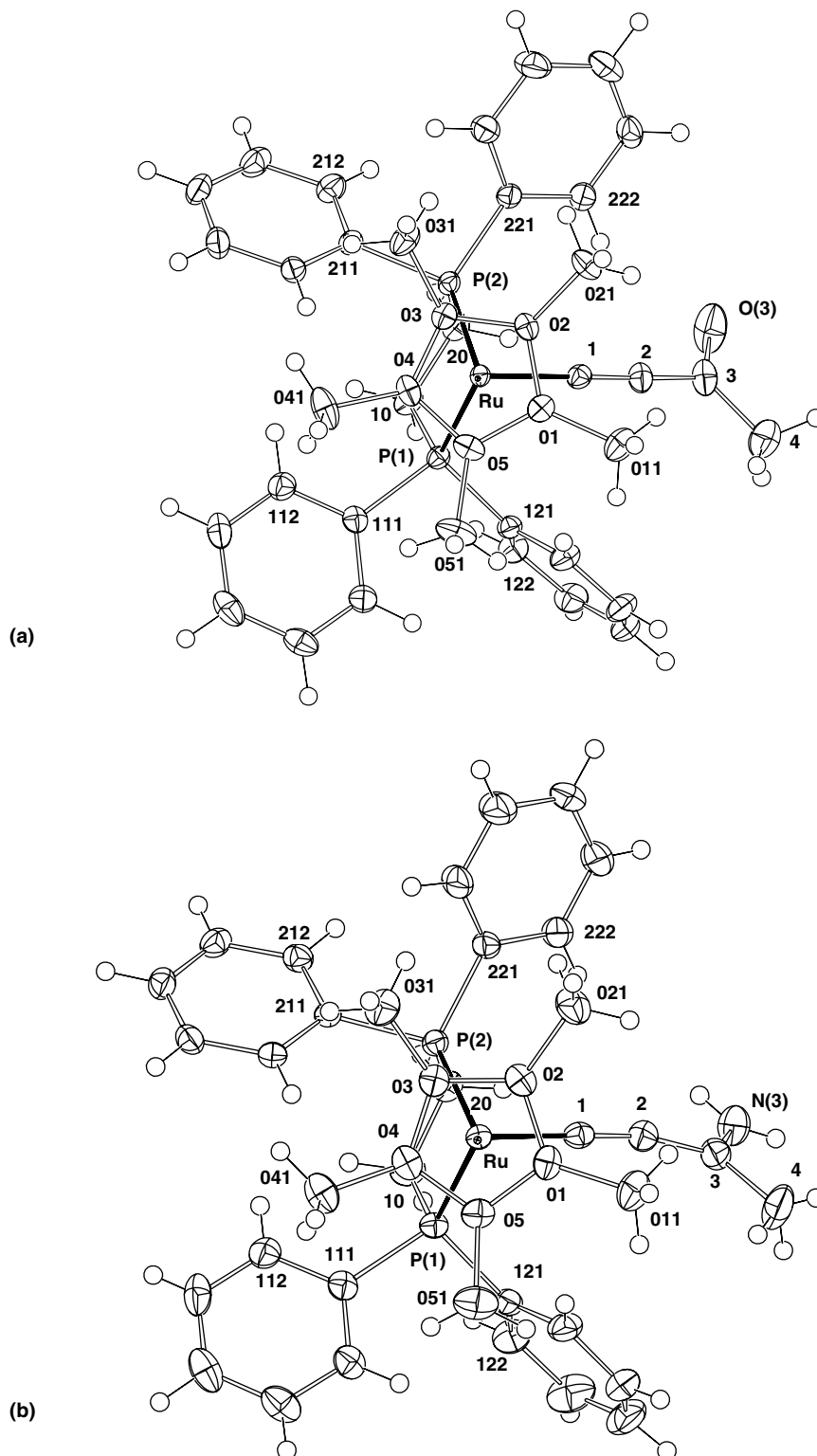


Fig. 1. Plots of (a) a molecule of $\text{Ru}\{\text{C}=\text{CC}(\text{O})\text{Me}\}(\text{dppe})\text{Cp}^*$ (**3**) and (b) the cation of $[\text{Ru}\{\text{C}\equiv\text{CC}(\text{=NH}_2)\text{Me}\}(\text{dppe})\text{Cp}^*]\text{PF}_6$ (**4**).

been unable to make this complex by any rational approach, so that full characterisation, including spectroscopic studies, has not been possible. However, the structural data (below), including the short Ru–C(1) separation [1.929(6) Å], are consistent with delocalisation of the positive charge across the C₇ ligand as indicated in Scheme 3.

Complexes **5** and **6** are closely related to those of the analogous compounds **7** and **8** described by Dixneuf and coworkers [15]. These were both obtained from *trans*-RuCl(C≡CC≡CH)(dppe)₂, the former by reaction of the diyne with the allenylidenes [RuCl(=C=C=C=CR¹CH₂R²)(dppe)₂]⁺ (R¹ = Me, R² = H; R¹ = Ph, R² = H, Me), while **8** was formed by oxidation of the diyne with [FeCp₂]PF₆.

2.3. X-ray structure determinations

The X-ray determined structures of complexes **3–6** are shown in Figs 1–4 and selected structural parameters are presented in Table 1. The common Ru(dppe)Cp* fragments are similar to others reported on earlier occasions [9,10] and are characterised by Ru–P and mean Ru–C(Cp*) distances of between 2.2684–2.2910(8) and 2.25–2.26 Å, respectively, with P–Ru–P and P(1,2)–Ru–C(1) angles of between 82.70–83.67(6)°, and 79.5–88.8(2)°, respectively. These values are all consistent with pseudo-octahedral coordination about the Ru atom.

The structural data for **3** [Fig. 1(a)] are in agreement with a major contribution from **3a** to the molecular structure, with values for Ru–C(1) [1.979(3) Å] and C(1)–C(2) [1.223(4) Å] close to those expected for Ru–C single and C≡C triple bonds and similar to those found in Ru{C≡CC(O)Me}(PPh₃)₂Cp [11b]. The Ru₃ unit adopts an almost linear arrangement with angles at C(1) and C(2) of 179.4(2)° and 170.1(2)°, respectively (see Table 2).

The cation of complex **4** [Fig. 1(b)] has relatively short Ru–C [1.942(3) Å] and long C≡C triple bonds [1.238(4) Å] [compared with expected values of 2.01 (Ru–C), 1.85 (Ru=C), 1.20 (C≡C), 1.31 Å (C=C)] while, within the remainder of the ligand, C(3)–C(2,4) distances are 1.382 and 1.511(6) Å and the C(3)–N(3) distance [1.307(4) Å]. Again, these data are consistent with a degree of multiple bonding intermediate between forms **4a** and **4b**.

The structure proposed for **5** is consistent with an X-ray study on crystals obtained by the slow diffusion of hexane into a concentrated acetone solution. The crystal is modelled in terms of only the *Z* isomer (Fig. 2), disposed about a crystallographic inversion centre so that two superimposed orientations of the centre string with common Ru(dppe)Cp* sites are present. In fact, the two arrangements are not strictly superimposed since the Ru–C(1)–C(2)–C(3) sequence is not linear [as required for a formulation where there

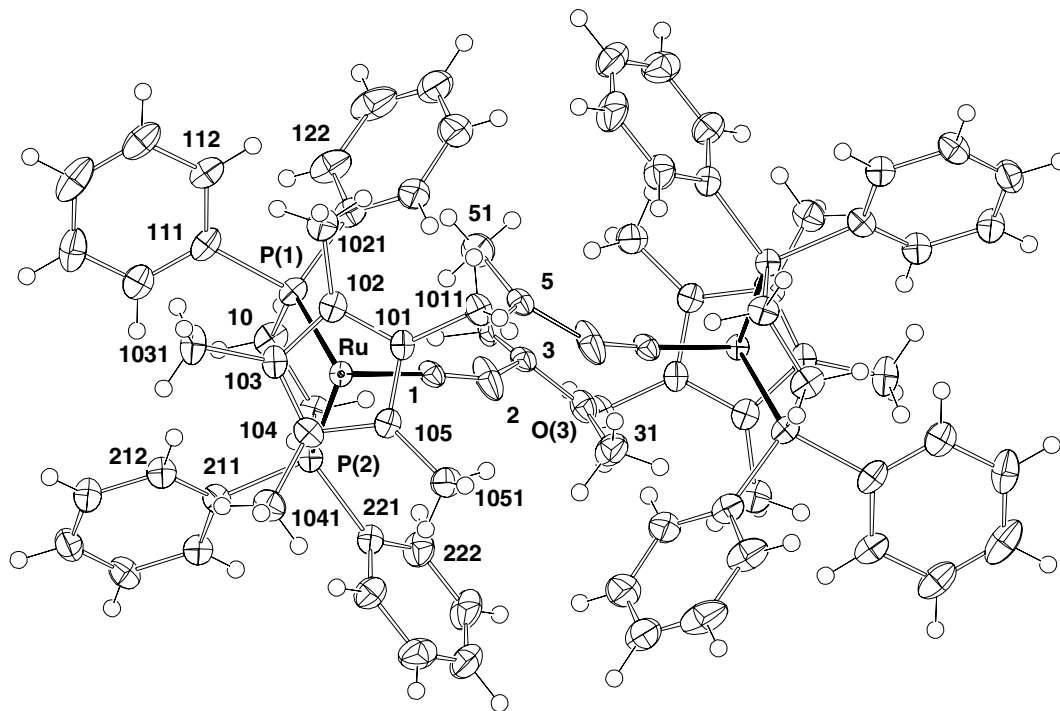


Fig. 2. Plot of a cation in [*Z*{Cp*(dppe)Ru}C≡CC(OMe)=CHCMe=C=C={Ru(dppe)Cp*}]PF₆ (**5**) (one disordered component; the superimposed aggregate is centrosymmetric).

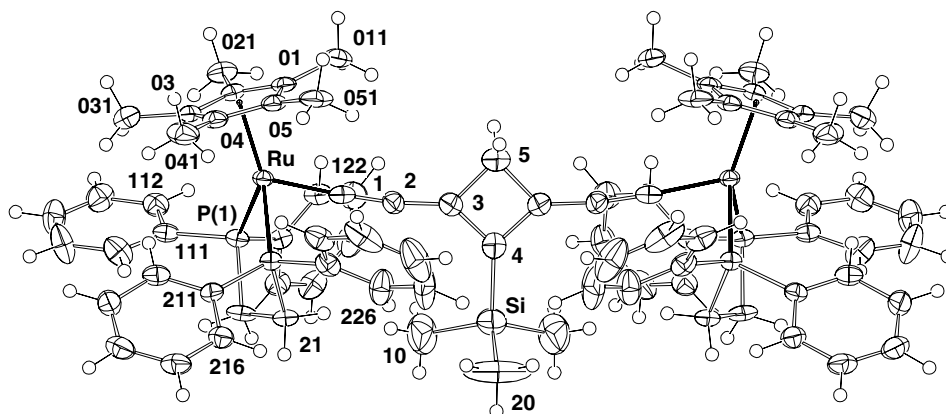


Fig. 3. Plot of the cation in $[\{\text{Ru}(\text{dppe})\text{Cp}^*\}_2\{\mu\text{-C}\equiv\text{CC}_4\text{H}_2(\text{SiMe}_3)\text{C}\equiv\text{C}\}]\text{PF}_6$ (**6**).

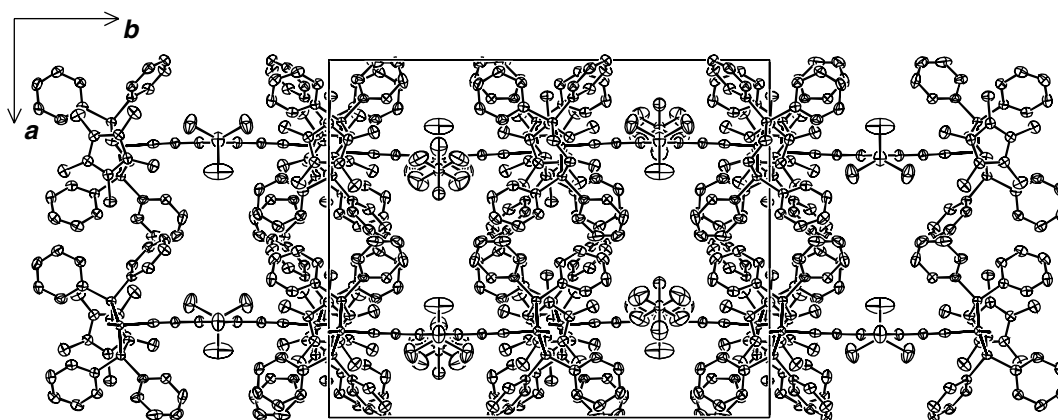


Fig. 4. Plot of the unit cell contents of **6**, projected down c .

is a triple bond between atoms C(1)–C(2)], while the elongated displacement ellipsoid for C(2) suggests that two sites for this atom are unresolved. Further, there are two components assigned as C(4) and O(3), which are separated by 0.3 Å, consistent with the two occupancies depicted in Chart 1. The results of the structure determination are consistent with the proposed highly delocalised nature of the C₇ bridging ligand [C–C distances 1.214(6) and between 1.38 and 1.43(1) Å for C(3)–C(5)] and the presence of the pendant groups OMe, Me and H. The two ruthenium centres are attached to the hydrocarbon by Ru–C bonds [1.944(4) Å] which are intermediate between Ru–C(sp) (alkynyl) and Ru=C(sp²) (vinylidene) lengths. Along the chain, the C–C separations are 1.214(6), 1.502(10), 1.403(14) and 1.400(13) Å. The angle at C(1) is close to linear [176.1(4)°], while those at C(2) and C(3) are respectively 144.9(7) and 127.9(7)°, resulting in apparent bending of the chain, presumably an artefact of the disorder mentioned above.

Crystals of $[\{\text{Ru}(\text{dppe})\text{Cp}^*\}_2\{\mu\text{-C}\equiv\text{CC}_4\text{H}_2(\text{SiMe}_3)\text{C}\equiv\text{C}\}]\text{PF}_6$ (**6**) contain a cation (Fig. 3) disposed astride a crystallographic mirror plane, modelled as a central cyclobutenylidene group substituted on C(4) by a SiMe₃ group and on C(3) and C(3') by two C≡CRu(dppe)Cp* fragments; an interesting crystal packing is found (Fig. 4), the anions and SiMe₃ groups being disposed about the crystallographic mirror plane at $y = 0.25, 0.75$, and the rutheniums and associated ligands disposed about $y = 0, 1/2$. The two Cp* ligands have a relative *cisoid* geometry about the two ruthenium atoms. Within the four-membered ring, C(3)–C(4) [1.44(1) Å] is shorter than C(3)–C(5) [1.50(1) Å], which is consistent with partial multiple bond character for the C(3)–C(4)–C(3') moiety. The bridging ligand is nearly linear and the four-membered ring is slightly distorted with the C(3)–C(4) and C(3)–C(5) bonds being marginally different. The separation C(1)–C(2) [1.229(6) Å] is somewhat long for a conventional C≡C triple bond and C(2)–C(3) [1.352(9) Å] short for a C(sp)–C(sp²) bond.

Table 1
Selected bond distances (Å) and angles (°)

	3	4	5	6
<i>Bond distances (Å)</i>				
Ru–P(1)	2.2830(6)	2.2910(8)	2.272(1)	2.282(2)
Ru–P(2)	2.2684(6)	2.2705(8)	2.281(1)	2.284(2)
Ru–C(Cp*) ^a	2.217–2.274(3)	2.226–2.285(3)	2.238–2.271(5)	2.234–2.290(6)
(av.)	2.25(2)	2.26(2)	2.257(14)	2.26(2)
Ru–C(0)	1.90 ₂	1.91 ₃	1.91 ₁	1.90 ₈
Ru–C(1)	1.979(3)	1.942(3)	1.944(4)	1.929(6)
C(1)–C(2)	1.223(4)	1.238(4)	1.214(6)	1.229(9)
C(2)–C(3)	1.442(4)	1.382(4)	1.502(10)	1.352(9)
C(3)–C(4)	1.492(5)	1.511(5)	1.403(14)	1.44(1)
C(3)–X(3)	1.233(4) [O]	1.307(4) [N]	1.401(9) [O]	
<i>Bond angles (°)</i>				
P(1)–Ru–P(2)	83.11(2)	82.70(3)	82.95(4)	83.67(6)
P(1)–Ru–C(1)	84.73(6)	85.14(9)	87.7(1)	88.8(2)
P(2)–Ru–C(1)	82.79(7)	85.01(9)	79.5(1)	81.9(2)
C(0)–Ru–P(1)	134. ₁	132. ₇	131. ₁	132. ₀
C(0)–Ru–P(2)	132. ₉	132. ₁	135. ₀	133. ₃
C(0)–Ru–C(1)	121. ₄	122. ₆	123. ₀	120. ₇
Ru–C(1)–C(2)	179.4(2)	178.4(3)	176.1(4)	176.3(5)
C(1)–C(2)–C(3)	170.1(2)	167.6(3)	144.9(7)	172.6(7)
C(2)–C(3)–C(4)	117.2(3)	120.4(3)	127.9(7)	138.3(6)
C(2)–C(3)–X(3)	121.6(3) [O(3)]	122.0(3) [N(3)]	112.5(7) [O(3)]	131.6(6) [C(5)]
C(4)–C(3)–X(3)	121.2 [O(3)]	117.6(3) [N(3)]	111.9(7) [O(3)]	90.0(6) [C(5)]
C(3)–C(4)–X			129.4(7) [C(5)]	133.5(4) [Si]

For **5**: C(5)–C(51) 1.498(14) Å; C(1)–C(2)–C(5') 150.9(6), C(2',4)–C(5)–C(51) 124.4, 121.3(7)° (primes denoting inversion images). For **6**: C(3)–C(5) 1.50(1), C(4)–Si 1.89(1) Å; C(3)–C(4,5)–C(3') 92.4, 87.5(7)°.

^a In no case is the wide range a consequence of a random distribution but, rather, a tilt of the ring plane toward the organic donor, as indicated by the C(0)–Ru–X angles [C(0) is the centre of the C₅ ring].

Table 2
Crystal data and refinement details

Compound	3	4	5	6
Formula	C ₄₀ H ₄₂ OP ₂ Ru	C ₄₀ H ₄₄ F ₆ NP ₃ Ru	C ₈₁ H ₈₅ F ₆ OP ₅ Ru ₂ · 2C ₃ H ₆ O	C ₈₃ H ₈₉ F ₆ P ₅ Ru ₂ Si
MW	701.8	846.8	1661.7	1585.7
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>P2₁/n</i> (#14)	<i>P2₁/c</i> (#14)	<i>C2/c</i> (#15)	<i>Pnma</i> (#62)
<i>a</i> (Å)	10.3938(6)	13.639(2)	29.315(5)	19.854(2)
<i>b</i> (Å)	23.172(1)	14.919(2)	16.232(3)	24.463(2)
<i>c</i> (Å)	14.8125(9)	18.509(3)	17.833(3)	17.122(1)
β (°)	109.612(2)	92.488(2)	110.761(3)	
<i>V</i> (Å ³)	3360	3763	7935	8316
<i>Z</i>	4	4	4	4
<i>D_c</i> (g cm ⁻³)	1.38 ₇	1.49 ₅	1.39 ₁	1.26 ₆
μ (cm ⁻¹)	5.9	6.0	5.4	5.3
Crystal size (mm)	0.35 × 0.12 × 0.10	0.25 × 0.20 × 0.10	0.28 × 0.28 × 0.11	0.12 × 0.10 × 0.07
<i>T</i> _{min/max}	0.90	0.84	0.83	0.81
2 θ _{max} (°)	58	58	53	58
<i>N</i> _{tot}	67,792	44,059	39,745	128,813
<i>N</i> (<i>R</i> _{int})	17514 (0.084)	9535 (0.047)	7855 (0.058)	17302 (0.15)
<i>N</i> _o	9499	6834	6486	6322
<i>R</i>	0.044	0.038	0.058	0.053
<i>R_w</i> (<i>n</i>) _w	0.040 (0.4)	0.039 (0.4)	0.058 (3)	0.061 (0.4)

2.4. Electrochemistry

The cyclic voltammogram of **3** shows a single reversible reduction at $E = -1.31$ V and two oxidation waves at $E = +0.53$ V (reversible) and at $E^{\text{pa}} = +1.06$

V (irreversible) (under our conditions, the FeCp₂/[FeCp₂]⁺ couple is found at +0.46 V). This electrochemical behaviour is in accord with related complexes recently reported [15b]. The initial oxidation of **3** is presumably metal-centred, involving a Ru(II)/Ru(III)

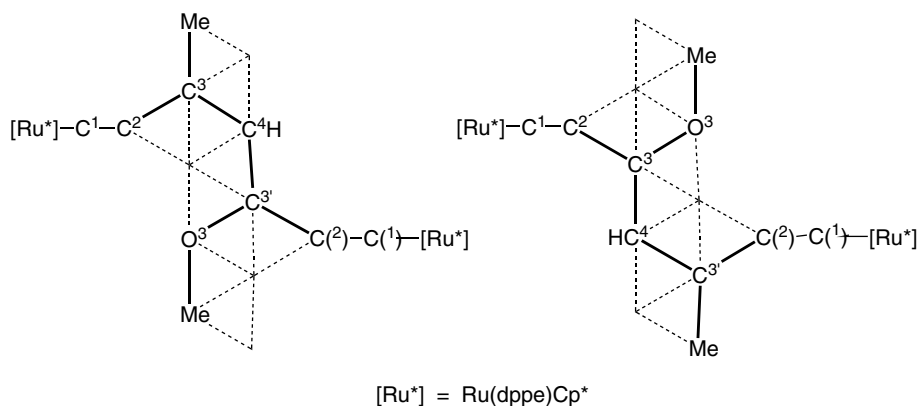


Chart 1.

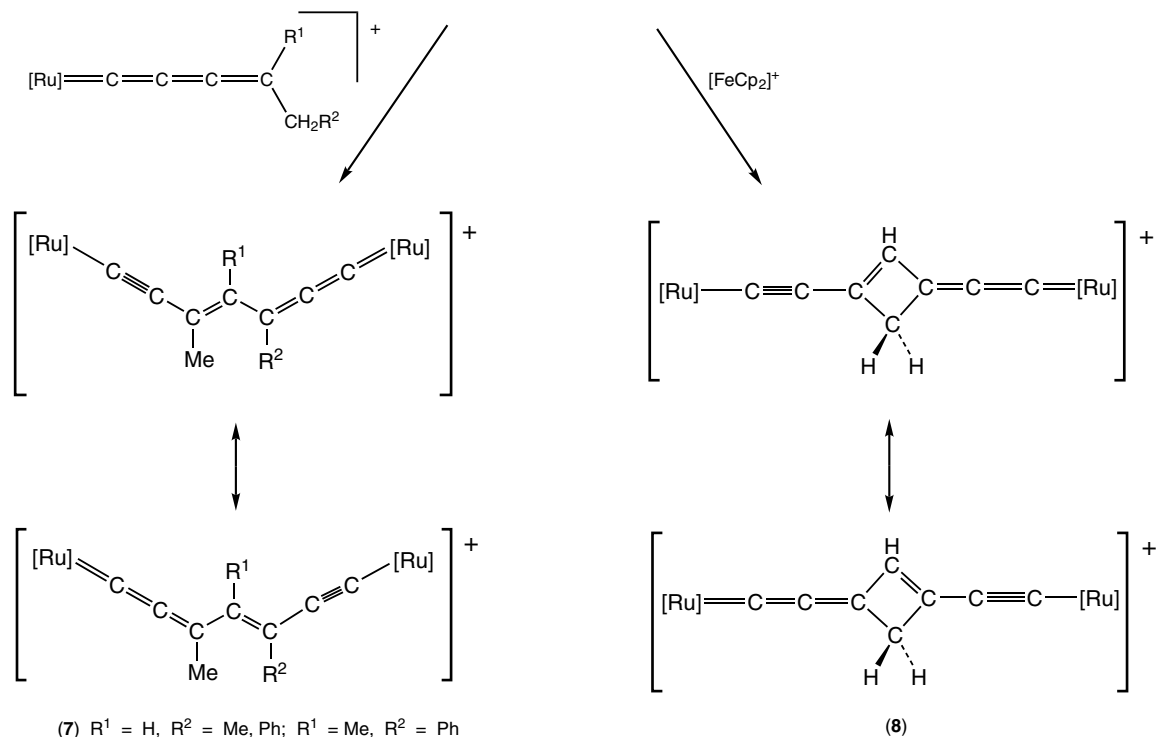
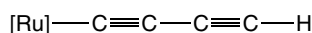
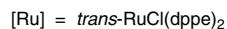
process, while the second irreversible wave is consistent with the higher oxidised species undergoing further chemical reactions. The well-defined single reduction process is attributed to reduction of the unsaturated C_7 ligand.

3. Discussion

Alkynyl complexes are strong bases and are readily protonated by the ammonium ion, for example, releasing free NH_3 . Further reaction of the latter does not

readily occur with vinylidenes in the $\text{Ru}(\text{PP})\text{Cp}'$ series, because the phenyl groups of the PPh_3 or dppe ligands present on the ruthenium centre afford steric protection to $\text{C}(1)$ and $\text{C}(2)$. Consequently, ready isolation of the cationic vinylidene complexes [1,16] occurs even in the presence of ammonium salts.

In contrast, the outer $\text{C}(3)$ and $\text{C}(4)$ atoms of butatrienylydene ligands are not so well protected. The chemistry of butatrienylydene ligands is well understood from both experimental and theoretical results, which show the carbon atoms have alternating electron-poor and electron-rich character as they extend



Scheme 4.

out from the metal centre [14,17,18]. The formation of all four complexes described here is ascribed to initial formation of the reactive butatrienylidene complex **A**, which subsequently reacts rapidly with various nucleophiles also present in the reaction mixture. Under the reaction conditions used here, desilylation of the protected diynes would generate $\text{HC}\equiv\text{CC}\equiv\text{CH}$ in situ, even when this reaction was performed in the absence of KF , where F^- formed by the hydrolysis of the PPF_6^- anion is the active reagent [19]. Coordination of the diyne to the ruthenium centre follows to give either **A** directly, or the diyne complex which can be protonated by the $[\text{NH}_4\text{Et}_3]^+$ or $[\text{NH}_4]^+$ cations also present [1,16].

Complex **3** is probably formed by nucleophilic attack of trace amounts of water on **A** to give the hydroxy(vinylidene) cation which then transforms into **3** via proton migration. A similar reaction of NH_3 with **A** would afford the analogous ammonium cation **4** (Scheme 1).

Complexes **5** and **6** have precedents in the chemistry of the closely related $\text{RuCl}(\text{dppe})_2$ system studied by Dixneuf and coworkers. They have described coupling of the neutral butadiynyl *trans*- $\text{RuCl}(\text{C}\equiv\text{CC}\equiv\text{CH})\text{-(dppe)}_2$ with the cationic allenylidenes *trans*- $[\text{RuCl}=\text{C}=\text{C}=\text{CR}^1(\text{CH}_2\text{R}^2)(\text{dppe})_2]^+$ (obtained from the corresponding propargylic alcohols) to give **7** ($\text{R} = \text{H}$, $\text{R}' = \text{Me}$, Ph ; $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$), and the formation of cyclobutenylidenium cations *trans*- $[\{\text{RuCl}(\text{dppe})_2\}_2\{\mu\text{-C}\equiv\text{CC}_4\text{H}_3\text{C}\equiv\text{C}\}]^+$ (**8**) by partial oxidation of *trans*- $\text{RuCl}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{dppe})_2$ with $[\text{FeCp}_2]^+$. The proposed routes to these derivatives involve (a) attack of the allenylidene at the $\text{C}_\gamma\equiv\text{C}_\delta$ triple bond of the diyne and (b) a metal-assisted [2 + 2] cycloaddition of two $\text{C}_\gamma\equiv\text{C}_\delta$ triple bonds of adjacent molecules (Scheme 4).

While it is attractive to incorporate these routes as a rationalisation of the formation of **5** and **6**, respectively, their structures reveal that subsequent reactions have also occurred. In neither reaction can we exclude formation and desilylation of intermediate SiMe_3 -containing complexes. However, we are inclined to propose that the reactive butatrienylidene **A** is attacked by methoxide to give **B**. Attack of the electron-rich CH_2 group at electrophilic C_γ of a second molecule of **A** affords binuclear intermediate **C**. From this, **5** is formed by an allylic hydrogen transfer (Scheme 2).

Complex **6** may be formed by the [2 + 2] cycloaddition of the $\text{C}(3)=\text{C}(4)$ double bond of the butatrienylidene **A** to the $\text{C}(3)-\text{C}(4)$ triple bond of $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{dppe})\text{Cp}^*$ formed in the reaction mixture (Scheme 3). Cycloaddition reactions between vinylidenes and acetylides are well known to generate four-membered cyclic systems [14,20–23]. However, at present, no [2 + 2] cycloaddition reactions at the $\text{C}(3)-\text{C}(4)$ double bond of an isolated butatrienylidene

have been reported. Unfortunately, we have not been able to confirm this reaction pathway by, for example, protonation of the butadiynyl complex followed by addition of a second equivalent of the diyne complex. While the reaction mixture rapidly acquires the deep blue colour of **6**, attempted purification of this material gave only mixtures of as yet unidentified complexes, although the mass spectrum of the solid product contains an ion at m/z 1440, consistent with the presence of **6** (or an isomeric product). While the small amount of **6** obtained may also be consistent with its being formed by oxidation by traces of air, we have been able to obtain neither **6** nor any related species by partial chemical oxidation of $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CR})(\text{dppe})\text{Cp}^*$ ($\text{R} = \text{H}$, SiMe_3) with $[\text{FeCp}_2]^+$.

4. Conclusion

Several products have been isolated during attempts to make the diyne complexes $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CR})\text{-(dppe)Cp}^*$ ($\text{R} = \text{H}$ or SiMe_3). A combination of X-ray structural studies with IR and NMR spectroscopy has enabled their formulation as the acyl complex **3** and the imido cation **4**, both containing C_4 chains, and the butenyneallenylidene **5** and the bis(ethynyl)cyclobutenylidene **6**, containing C_7 chains, linking the two metal centres. Plausible reaction pathways which might lead to these compounds involving the intermediacy of butatrienylidene **A** in each case are discussed.

5. Experimental

5.1. General experimental conditions

All reactions were carried out under dry, high purity argon using standard Schlenk techniques. Common solvents were dried, distilled under argon and degassed before use.

5.2. Instrumentation

Infrared spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Nujol mull spectra were obtained from samples mounted between NaCl discs. NMR spectra were recorded on Bruker ACP300 instrument (^1H at 300.13 MHz, ^{13}C at 75.47 MHz, ^{31}P at 121.503 MHz). Samples were dissolved in CDCl_3 , unless otherwise stated, contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for ^1H and ^{13}C NMR spectra and external H_3PO_4 for ^{31}P NMR spectra. ES mass spectra: VG Platform 2 or Finnigan LCQ. Solutions were directly infused into the instrument. Chemical aids to ionisation were used as required [24]. Cyclic voltammograms were recorded using

a PAR model 263 apparatus, a saturated calomel electrode, and ferrocene as internal calibrant ($\text{FeCp}_2/\text{[FeCp}_2\text{]}^+ = +0.46$ V). Elemental analyses were performed at CMAS, Belmont, Australia.

5.3. Reagents

$\text{Na[BPh}_4\text{]}$ (Aldrich), and $[\text{NBu}_4]\text{F}$ (Aldrich) were used as received. The compounds $\text{RuCl(PPh}_3)_2\text{Cp}$ [25], RuCl(dppe)Cp^* [9b], $[\text{FeCp}_2]\text{PF}_6$ [26], $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3$ [27] and $\text{SiMe}_3\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3$ [28] were prepared using the cited methods.

5.3.1. $\text{Ru}\{\text{C}\equiv\text{CC}(\text{OMe})\}(\text{dppe})\text{Cp}^*$ (**3**)

$\text{HC}\equiv\text{CC}\equiv\text{CSiMe}_3$ (78 mg, 0.60 mmol) was added to a suspension of **1** (200 mg, 0.30 mmol) and $[\text{NH}_4]\text{PF}_6$ (98 mg, 0.60 mmol) in MeOH (10 ml) and the mixture was stirred at r.t. for 3 h. Solvent was removed and the residue extracted in CH_2Cl_2 and loaded onto a basic alumina column (20 × 2 cm). Elution with Et_2O gave a light yellow band containing $\text{Ru}\{\text{C}\equiv\text{CC}(\text{OMe})\}(\text{dppe})\text{Cp}^*$ (**3**) (106 mg, 50%). Anal. Calcd ($\text{C}_{40}\text{H}_{42}\text{P}_2\text{ORu}$): C, 68.46; H, 5.96; *M*, 702. Found: C, 68.57; H, 6.08. IR (nujol): $\nu(\text{CC})$ 2024m, 2006s; $\nu(\text{C}=\text{O})$ 1605s cm^{-1} . ^1H NMR: δ 1.59 (s, 15H, Cp^*), 1.89 (s, 3H, Me), 2.18, 2.78 (2m, 2 × 2H, CH_2CH_2), 7.20–7.71 (m, 20H, Ph). ^{13}C NMR: δ 9.78 (s, C_5Me_5), 29.11 (m, CH_2CH_2), 32.37 (s, Me), 93.71 (s, C_5Me_5), 118.88 (s, C_2), 127.07–137.85 (m, Ph), 159.24 [t, 2J (CP) 23 Hz, C_1], 180.89 (s, CO). ^{31}P NMR: δ 80.81 (s, dppe). ES-MS (MeOH, *m/z*): 703, $[\text{M} + \text{H}]^+$; 635, $[\text{Ru}(\text{dppe})\text{Cp}^*]^+$.

5.4. $[\text{Ru}\{\text{C}\equiv\text{CC}(\text{=NH}_2\text{Me})\}(\text{dppe})\text{Cp}^*]\text{PF}_6$ (**4**)

Complex **1** (290 mg, 0.43 mmol), $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$ (84 mg, 0.43 mmol), KF (25 mg, 0.43 mmol) and $[\text{NH}_4]\text{PF}_6$ (141 mg, 0.86 mmol) were dried under vacuum for 10 min. MeOH (30 mL) was added and the solution was heated at reflux point for 1 h, after which the solvent was removed and the residue extracted in CH_2Cl_2 and loaded onto preparative t.l.c. plates. Development with acetone-hexane (1/1) gave a bright yellow band (R_f 0.6) that was crystallised from $\text{CH}_2\text{Cl}_2/\text{hexane}$ to give $[\text{RuC}\equiv\text{CC}(\text{=NH}_2)\text{Me}(\text{dppe})\text{Cp}^*]\text{PF}_6$ (**4**) (245 mg, 67%). Anal. Calcd ($\text{C}_{40}\text{H}_{44}\text{F}_6\text{NP}_3\text{Ru}$): C, 56.73; H, 5.24; N, 1.65; *M*, 702 (cation). Found: C, 56.60; H, 5.21; N, 1.58. IR (nujol): $\nu(\text{NH})$ 3449w, 3357w, 3271w; $\nu(\text{CCC})$ 1982 (br); $\nu(\text{CN})$ 1651m; $\nu(\text{PF})$ 837s cm^{-1} . ^1H NMR: δ 1.54 [t, 3J (HP) 2 Hz, 15H, Cp^*], 1.77 (s, 3H, Me), 2.24, 2.64 (2m, 2 × 2H, CH_2CH_2), 7.39–7.47 (m, 20H, Ph). ^{13}C NMR: δ 9.76 (s, C_5Me_5), 26.15 (s, Me), 29.11 (m, PCH_2), 96.22 (s, C_5Me_5), 121.72 (s, C_1), 127.96–135.69 (m, Ph), 156.74 [s, $\text{C}(\text{=NH}_2)$], 216.37 [t, 2J (CP) 20 Hz, C_2]. ^{31}P NMR: δ -143.5 (septet, PF_6^-), 80.30 (s, dppe). ES-MS (*m/z*): 702, M^+ ; 635, $[\text{Ru}(\text{dppe})\text{Cp}^*]^+$.

5.5. $[\{\text{Cp}^*(\text{dppe})\text{Ru}\}\{\text{C}\equiv\text{CC}(\text{OMe})=\text{CHCMe}=\text{C}=\text{C}\}\{\text{Ru}(\text{dppe})\text{Cp}^*\}]\text{PF}_6$ (**5**)

The blue fraction obtained with **3** was further purified by chromatography, elution with 1/9 acetone/diethyl ether giving a bright blue band that was chromatographed a second time, followed by crystallisation (acetone/hexane) to give bright blue crystals of $[\{\text{Cp}^*(\text{dppe})\text{Ru}\}\{\text{C}\equiv\text{CC}(\text{OMe})=\text{CHCMe}=\text{C}=\text{C}\}\{\text{Ru}(\text{dppe})\text{Cp}^*\}]\text{PF}_6$ (**5**) (57 mg, 12%). Anal. Calcd ($\text{C}_{81}\text{H}_{85}\text{F}_6\text{OP}_5\text{Ru}_2$): C, 62.95; H, 5.54. Found: C, 63.49; H, 5.27. IR (Nujol): $\nu(\text{CCC})$ 1959 s; $\nu(\text{PF})$ 841 s cm^{-1} . ES-MS (MeOH, *m/z*): 1401, M^+ ; 635, $[\text{Ru}(\text{dppe})\text{Cp}^*]^+$.

The NMR spectra contained peaks assigned to two isomers present in a 56/44 ratio. Major *E* isomer in CD_2Cl_2 : ^1H NMR: δ 1.69 (s, 3H, Me), 3.24 (s, 3H, OMe), 5.44 (s, 1H, CH). ^{13}C NMR: δ 10.18 (s, C_5Me_5), 26.17 (s, Me), 58.03 (s, OMe), 96.31, 97.04 (2s, C_5Me_5), 122.42 (s, C_4), 127.81 (s, C_2), 142.50 (s, C_5), 150.21 (s, C_6), 155.50 (s, C_3). ^{31}P NMR: δ 80.83 (s, dppe), 81.10 (s, dppe). Minor *Z* isomer: ^1H NMR: δ 1.47 (s, 3H, Me), 2.87 (s, 3H, OMe), 5.14 (s, 1H, CH). ^{13}C NMR: δ 10.14 (s, C_5Me_5), 31.81 (s, Me), 58.11 (s, OMe), 96.21, 96.84 (2s, C_5Me_5), 119.56 (s, C_4), 126.40 (s, C_2), 141.61 (s, C_5), 146.28 (s, C_6), 154.83 (s, C_3). ^{31}P NMR: δ 80.41 (s, dppe), 81.29 (s, dppe).

Peaks that could not be individually assigned: ^1H NMR: δ 1.58–1.62 (m, 4 × 15H, Cp^*), 2.29, 2.66 (br, 16H, CH_2CH_2), 7.21–7.68 (m, 80H, Ph). ^{13}C NMR: δ 29.66 (m, CH_2CH_2), 127.38–137.11 (m, Ph), 203.40 [t, 2J (CP) 22 Hz], 207.42 [t, 2J (CP) 20 Hz], 208.83 [t, 2J (CP) 21 Hz], 209.76 [t, 2J (CP) 22 Hz] (C_1 , C_7). ^{31}P NMR: δ -143.38 (septet, PF_6^-).

5.6. $[\{\text{Ru}(\text{dppe})\text{Cp}^*\}_2\{\mu\text{-C}\equiv\text{CC}_4\text{H}_2(\text{SiMe}_3)\text{C}=\text{C}\}]\text{PF}_6$ (**6**)

This complex was found as crystalline blocks in the solid obtained from attempts to isolate **5** from the products of reactions between **1** and $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$ (above).

6. Structure determinations

Full spheres of diffraction data to the indicated limits were measured at ca 153 K using a Bruker AXS CCD area-detector instrument. N_{tot} reflections were merged to *N* unique (R_{int} quoted) after “empirical”/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being used in the full matrix least squares refinement. All data were measured using monochromatic Mo- $K\alpha$ radiation, $\lambda = 0.71073$ Å. Anisotropic thermal parameter forms were refined for the non-hydrogen atoms, (*x*, *y*, *z*, U_{isoH} being constrained

at estimated values. Conventional residuals R , R_w on $|F|$ are given [weights: $(\sigma^2(F) + 0.000n_w F^2)^{-1}$ for n_w , see Table 2]. Neutral atom complex scattering factors were used; computation used the XTAL 3.7 program system [29]. Pertinent results are given in the Figures (which show non-hydrogen atoms with 50% probability amplitude displacement ellipsoids and hydrogen atoms with arbitrary radii of 0.1 Å) and tables.

6.1. Variata

4. $(x, y, z, U_{\text{iso}})_H$ were refined throughout.

5. As modelled in space group $C 2/c$, the molecules are disposed about crystallographic inversion centres, entailing superposition of disordered components in the string C(3)–C(51) and associated substituents. In particular, C(4), O(3) components were modelled as individual fragments, separated by 0.325(9) Å. Atom C(2), with an elongated displacement ellipsoid, in keeping with two closely disposed components, is unsusceptible to meaningful resolution and refinement as such.

6. The central methylene group was assigned as such in keeping with the chemistry, some uncertainty in the crystallographic assignment a concomitant of rather weak and meagre data.

7. Supplementary material

.cif files for the structure determinations (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre as CCDC 250010–250013 (complexes 3–6, respectively). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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