

Additions and intramolecular migrations of nucleophiles in cationic diruthenium μ -allenyl complexes

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Summary: the diruthenium μ -allenyl complex $[\text{Ru}_2(\text{CO})(\text{NCMe})(\mu\text{-CO})\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C(H)=C=C(Me)(Ph)\}(\text{Cp})_2\}][\text{BF}_4]$, **3b**, reacts with halide anions to yield the neutral derivatives $[\text{Ru}_2(\text{CO})_2(\text{X})\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C(H)=C=C(Me)(Ph)\}(\text{Cp})_2\}]$ [$\text{X} = \text{Cl}$, **4b**; $\text{X} = \text{Br}$, **4c**; $\text{X} = \text{I}$, **4d**]. Complex **4b** undergoes isomerization to the unprecedented bridging vinyl-chlorocarbene species $[\text{Ru}_2(\text{CO})(\mu\text{-CO})\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(Cl)C(H)=C(Me)(Ph)\}(\text{Cp})_2\}]$, **10**, upon filtration of a CH_2Cl_2 solution through an alumina column.

Complex **3b** reacts with an excess of NaBH_4 to give five products: the allene complex $[\text{Ru}_2(\text{CO})_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-CH}_2\text{=C=C(Me)(Ph)\}(\text{Cp})_2\}]$, **5**; the hydride species *trans*- $[\text{Ru}_2(\text{CO})_2(\mu\text{-H})\{\mu\text{-}\eta^1\text{:}\eta^2\text{-CH=C=C(Me)(Ph)\}(\text{Cp})_2\}]$, **6**, and *cis*- $[\text{Ru}_2(\text{CO})_2(\mu\text{-H})\{\mu\text{-}\eta^1\text{:}\eta^2\text{-CH=C=C(Me)(Ph)\}(\text{Cp})_2\}]$, **8**; the vinylalkylidene $[\text{Ru}_2(\text{CO})(\mu\text{-CO})\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(H)C(H)=C(Me)(Ph)\}(\text{Cp})_2\}]$, **9**; and the cluster $[\text{Ru}_3(\text{CO})_3(\mu\text{-H})_3(\text{Cp})_3]$, **7**.

Studies on the thermal stabilities of **5,6,8** and **9** have suggested a plausible mechanism for the formation of these complexes and for the synthesis of **10**.

Keywords: Diruthenium complexes; Allenyl; Bridging vinyl-chlorocarbene; Bridging hydride; Hydride migration

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Introduction

Allenyl ligands $[-C_{\alpha}(R)=C_{\beta}=C_{\gamma}(R')(R'')]$ coordinated in mono- [1], di- [1a, 2] and poly-nuclear complexes [1a, 3] have been the subject of much interest in recent years. In particular, di- and poly-nuclear species have attracted considerable attention: the unsaturated C_3 chain readily undergoes coupling reactions with organic fragments [4], providing an easy route for the synthesis of new multisite-bound hydrocarbyl ligands [1a, 2b, 4, 5].

Allenyls display a variety of coordination modes. The most common in dinuclear complexes is the $[\mu-\eta^1:\eta^2]$ fashion, with coordination through the C_{α} and C_{β} carbons [1a, 6]; however, alternative modes of coordination have been reported [1a, 2d, 7].

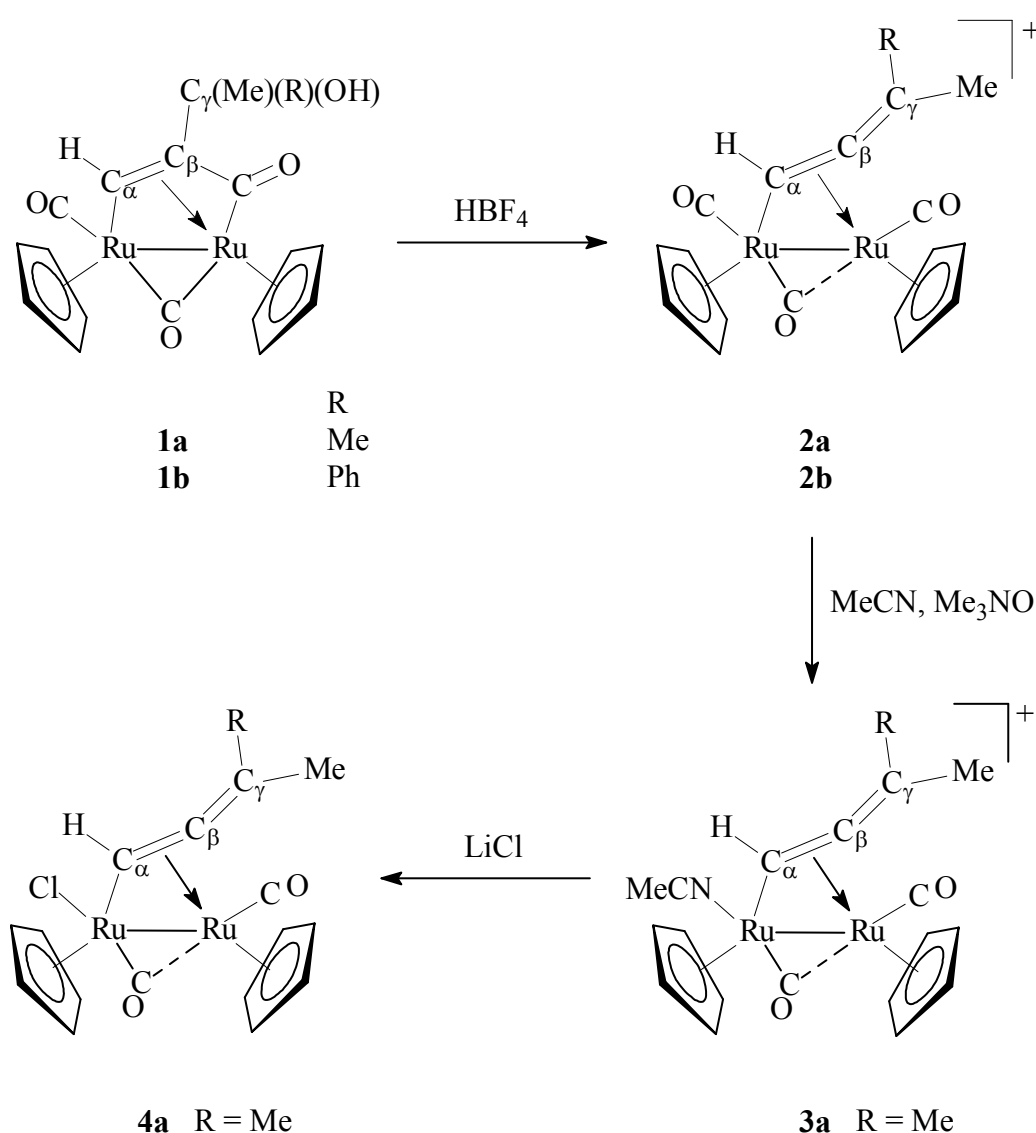
Common methods of synthesis include nucleophilic substitution on propargyl halides [8] and C-C bond formation by reaction with diazocompounds [9]. A further strategy for the preparation of $\mu-\eta^1:\eta^2$ allenyl complexes was recently reported [10], whereby the diruthenium complexes $[\text{Ru}_2(\text{CO})(\mu\text{-CO})\{\mu-\eta^1:\eta^3\text{-}C_{\alpha}(\text{H})C_{\beta}C_{\gamma}(\text{OH})(\text{Me})(\text{R})\text{C}(\text{O})\}(\text{Cp})_2]$ [R = Me, **1a**; R = Ph, **1b**], prepared from the cyclopentenone adduct $[\text{Ru}_2(\text{CO})(\mu\text{-CO})\{\mu-\eta^1:\eta^3\text{-}C(\text{Ph})C(\text{Ph})C(\text{O})\}(\text{Cp})_2]$ by alkyne exchange [11], are treated with HBF_4 , resulting in formation of the allenyl $[\text{Ru}_2(\text{CO})_2(\mu\text{-CO})\{\mu-\eta^1:\eta^2\text{-}C_{\alpha}(\text{H})=C_{\beta}=C_{\gamma}(\text{Me})(\text{R})\}(\text{Cp})_2][\text{BF}_4]$ [R = Me, **2a**; R = Ph, **2b**] (scheme 1) [12].

Preliminary studies on the chemistry of **2** have shown that the allenyl ligand is reactive towards neutral organic molecules such as alkynes and diazocompounds [12]. Moreover, compounds **2a-b** react readily with $\text{CH}_3\text{CN}/\text{Me}_3\text{NO}$ to give the acetonitrile adducts $[\text{Ru}_2(\text{CO})(\text{NCMe})(\mu\text{-CO})\{\mu-\eta^1:\eta^2\text{-}C(\text{H})=C=C(\text{Me})(\text{R})\}(\text{Cp})_2][\text{BF}_4]$ [R = Me, **3a**; R = Ph, **3b**], see scheme 1.

The chemistry of the derivatives **3** offers promise in that acetonitrile often acts as a labile ligand in organometallic chemistry. For dinuclear species acetonitrile removal is a crucial step in allowing coordination, at one of the two metal centres, of either anionic nucleophiles such as hydride, halides and pseudo-halides [13], or neutral organic fragments [14]. In a number of cases this substitution is the precursor of an intramolecular coupling reaction involving the species introduced and the pre-existing bridging hydrocarbyl ligand; these reactions, particularly those leading to carbon-carbon bond formation, have attracted interest because they may act as models for heterogeneously catalyzed processes occurring on metal surfaces [14a,e].

It has been previously demonstrated that complex **3a** undergoes nucleophilic substitution under mild conditions by chloride ion, towards which **2a-b** are completely unreactive, affording the neutral allenyl derivative $[\text{Ru}_2(\text{CO})_2(\text{Cl})\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C(H)=C=Me}\}(\text{Cp})_2]$, **4a** (scheme 1), the structure of which has been determined by X ray diffraction [12]. We report herein our studies on the reactivity of **3b** towards hydride and halide ions, aimed at exploring the possibility of coupling reactions between the allenyl ligand and species introduced to the metal centre by nitrile removal.

Scheme 1

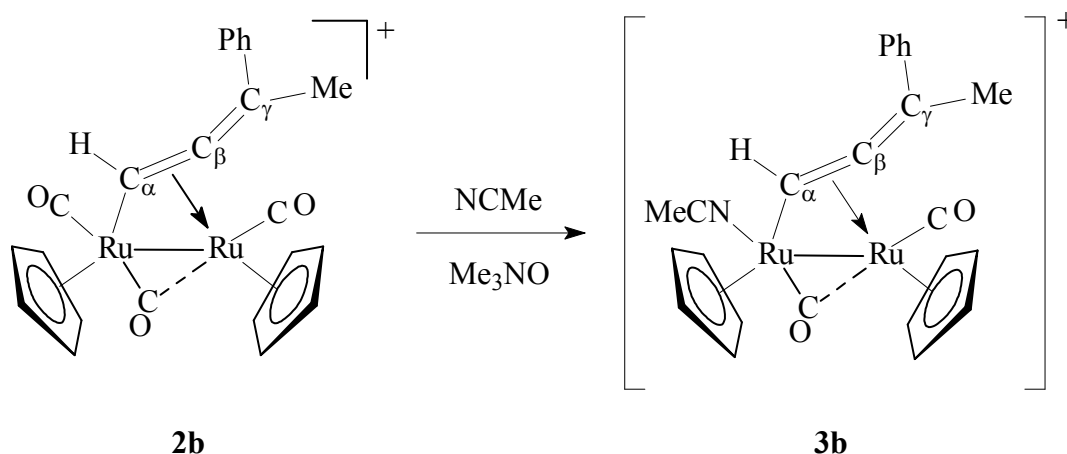


Results and discussion

1. Reactivity of acetonitrile derivatives of diruthenium allenyl complexes with NaBH₄

The acetonitrile compound $[\text{Ru}_2(\text{CO})(\text{NCMe})(\mu\text{-CO})\{\mu\text{-}\eta^1:\eta^2\text{-C(H)=C=C(Me)(Ph)\}(\text{Cp})_2\}][\text{BF}_4]$, **3b**, is obtained rapidly by treating a dichloromethane solution of **2b** with one equivalent of Me₃NO dissolved in acetonitrile (scheme 2).

Scheme 2

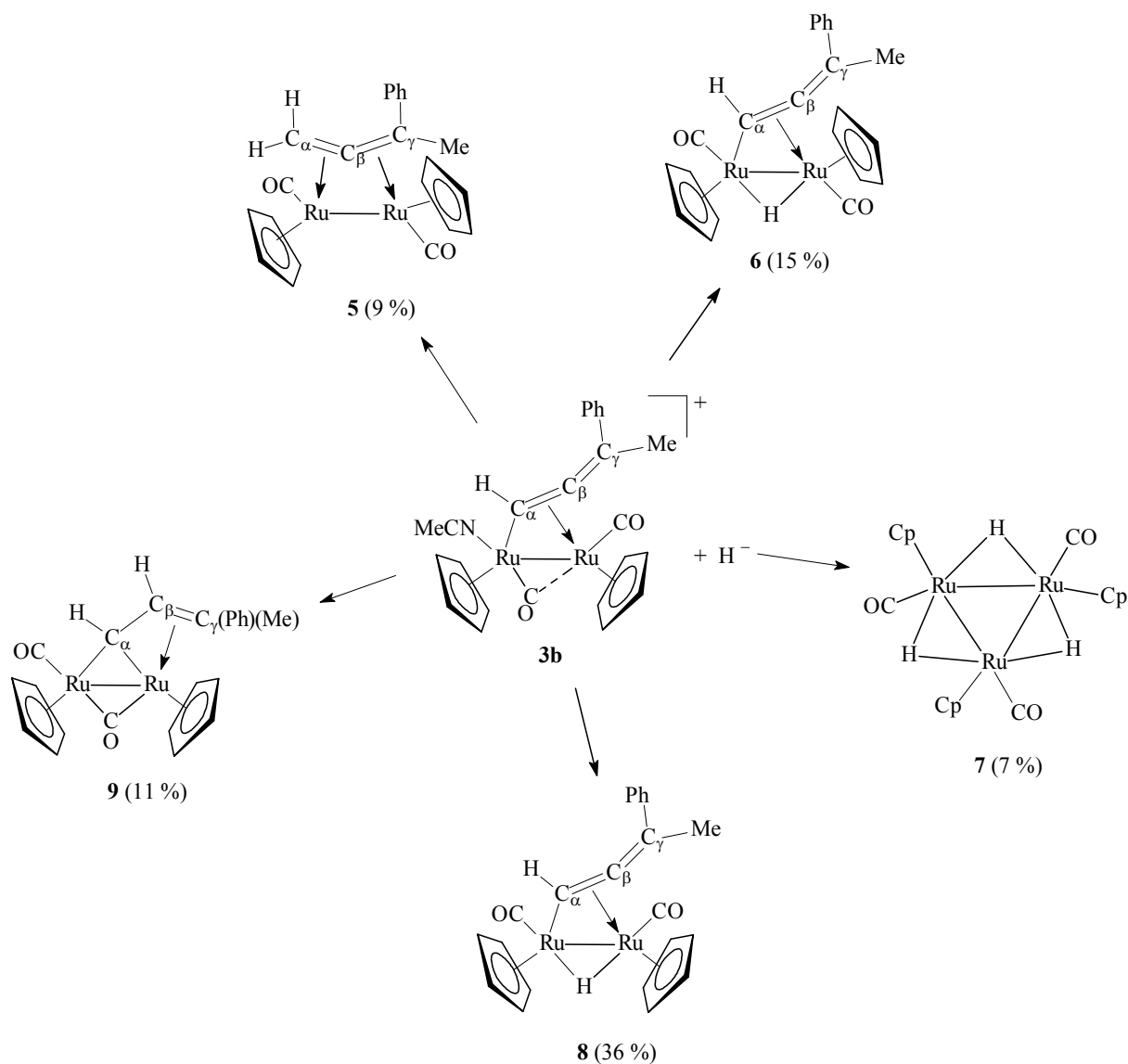


Complex **3b** was characterized by IR spectroscopy and used *in situ* for subsequent reactions with nucleophiles. The IR spectrum of **3b** (in CH₂Cl₂ solution) shows two bands at 2005 and 1870 cm⁻¹, corresponding to the presence of one terminal and one semi-bridging carbonyl ligands respectively. Complex **3b** probably exists as mixtures of interconverting isomers, due to σ,π and *cis/trans* fluxionality [10, 12], allowing the NCMe ligand to be bound at either ruthenium atom.

The reaction of **3b**, in THF solution, with NaBH₄ was investigated. IR spectroscopy revealed, after one hour, the complete disappearance of the starting material, and subsequent removal of the solvent gave a yellow-brown residue. The IR spectrum of this (in CH₂Cl₂ solution) exhibited two absorptions at 1981 cm⁻¹ (s) and 1919 cm⁻¹ (vs). The residue was chromatographed on an alumina column maintained at -35 °C, leading to the separation of five products (see scheme 3): $[\text{Ru}_2(\text{CO})_2\{\mu\text{-}\eta^2:\eta^2\text{-CH}_2\text{=C=C(Me)(Ph)\}(\text{Cp})_2\}]$, **5**; *trans*- $[\text{Ru}_2(\text{CO})_2(\mu\text{-H})\{\mu\text{-}\eta^1:\eta^2\text{-CH=C=C(Me)(Ph)\}(\text{Cp})_2\}]$, **6**; $[\text{Ru}_3(\text{CO})_3(\mu\text{-H})_3(\text{Cp})_3]$, **7**; *cis*- $[\text{Ru}_2(\text{CO})_2(\mu\text{-H})\{\mu\text{-}\eta^1:\eta^2\text{-CH=C=C(Me)(Ph)\}(\text{Cp})_2\}]$, **8**; and $[\text{Ru}_2(\text{CO})(\mu\text{-CO})\{\mu\text{-}\eta^1:\eta^3\text{-C(H)C(H)=C(Me)(Ph)\}(\text{Cp})_2\}]$, **9**. Complex **7**, the formation of which appears to be the

consequence of some fragmentation (yield 7 %), is a known species [15], and was identified by IR spectroscopy and mass spectrometry, in addition to its characteristic deep blue colour. The new compounds **5**, **6**, **8** and **9** have been fully characterized by IR and NMR spectroscopy, elemental analysis and mass spectrometry.

Scheme 3

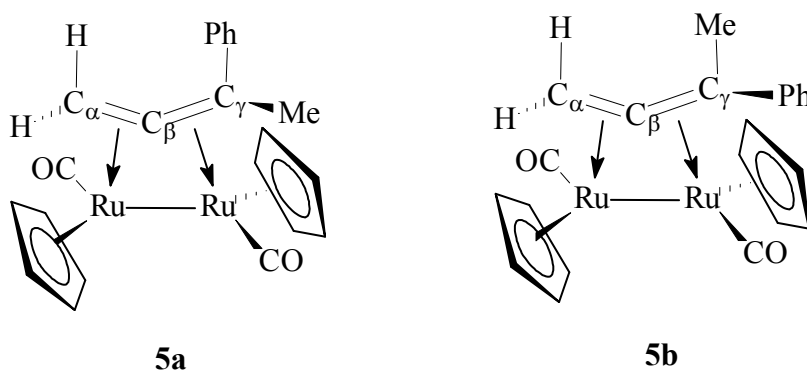


Complex **5** is the formal result of nitrile displacement and hydride attack on the C_α carbon of the allenyl unit of **3b**. The complex consists of a $[\text{Ru}_2(\text{Cp})_2(\text{CO})_2]$ core, with the two carbonyls occupying terminal sites at each metallic centre, and an allene ligand which is

coordinated to the ruthenium atoms through its π bonds. Dinuclear compounds containing the $\mu\text{-}\eta^2\text{:}\eta^2$ allene moiety have been described [16], some containing the $[\text{M}_2(\text{Cp})_2(\text{CO})_2]$ skeleton ($\text{M} = \text{Ru}$ [17], Fe [18]). Furthermore, the same $\eta^2\text{:}\eta^2$ allene ligand has also been reported to be coordinated in polynuclear species [19].

The spectroscopic data for **5** are characteristic of its diiron and diruthenium analogues. The IR spectrum (in CH_2Cl_2 solution) exhibits two carbonyl bands, at 1933 and 1915 cm^{-1} . The ^1H NMR spectrum shows the presence in solution of two isomers in comparable amounts. In analogous compounds the only configuration exhibited by the Cp ligands is *trans*, and it is likely that this is also the case here. For example, the complex $[\text{Ru}_2(\text{CO})_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_\alpha(\text{H})(\text{CO}_2\text{Et})=\text{C}_\beta=\text{C}_\gamma(\text{H})(\text{CO}_2\text{Me})\}(\text{Cp})_2]$ has been shown to exist in two *trans* forms, both characterized by X ray diffraction [17]. The two forms differed in the orientations of the substituents at C_γ , with one isomer having the CO_2Me group and the $\text{C}_\alpha\text{-H}$ in axial and equatorial sites, respectively, with regard to the Ru-Ru bond axis, while in the other the CO_2Me and the $\text{C}_\alpha\text{-H}$ lie in equatorial and axial positions, respectively. In both isomers, the CO_2Et function is in an axial position. On this basis, it is likely that the two isomers of **5** have the structures **5a** and **5b**, in which the orientations of the C_γ substituents (Ph and Me) are different. The ^1H NMR data suggest that in **5a** Ph is axial and Me is equatorial, whereas in **5b** the opposite configuration is adopted. Indeed, in the ^1H NMR spectrum of **5a** the methyl group (δ 1.82 ppm) is shielded compared with that in **5b** (δ 2.17 ppm), while the opposite trend is seen for the Cp resonances [**5a**: δ 5.04, 4.87 ppm; **5b** δ 4.65, 4.35 ppm]. These features indicate that the Me group is close to the Ru-Ru axis in **5a** while in **5b** it is oriented away from it (scheme 4).

Scheme 4



The C $_{\alpha}$ -H protons of **5** resonate as doublets at *ca.* 3.6 and 2.7 ppm, with a coupling constant of *ca.* 4 Hz. In the ^{13}C NMR spectrum, the C $_{\alpha}$ resonance is shifted significantly upfield (*e.g.* for **5b** at 29.7 ppm) with respect to complex **2b** [12], as a consequence of the loss of alkylidene character. The C $_{\beta}$ and C $_{\gamma}$ resonances occur at *ca.* 190 and 60 ppm.

Complexes **6** and **8**, the latter being the highest yield product (36 %), derive from **3b** by nitrile displacement with hydride ion, followed by rearrangement without involving the allenyl ligand.

The IR spectrum of **6** exhibits two carbonyl bands, at 1972 and 1918 cm $^{-1}$, with the second more intense than the first. Conversely, the IR spectrum of **8** shows bands at 1984 and 1921 cm $^{-1}$, with the latter being less intense than the former.

The NMR spectra of **6** and **8** reveal the absence of fluxionality and contain single sets of resonances. In the ^1H NMR spectra, the bridging hydrides are at typically high field chemical shifts, at -13.73 ppm (**6**) and -14.20 ppm (**8**). The salient ^1H and ^{13}C NMR features of **6** and **8** do not differ significantly from the data available for the parent **2b**. Thus, the C $_{\alpha}$ -H proton resonates as a quartet (due to coupling with C $_{\gamma}$ -Me) at 8.80 ppm (**6**) and 9.12 ppm (**8**). Moreover, the C $_{\alpha}$, C $_{\beta}$ and C $_{\gamma}$ carbons are observed at *ca.* 115, 165 and 110 ppm respectively. The CO carbons resonate at values typical of terminal carbonyl ligands (*e.g.* for **6** at 202.4 and 203.1 ppm).

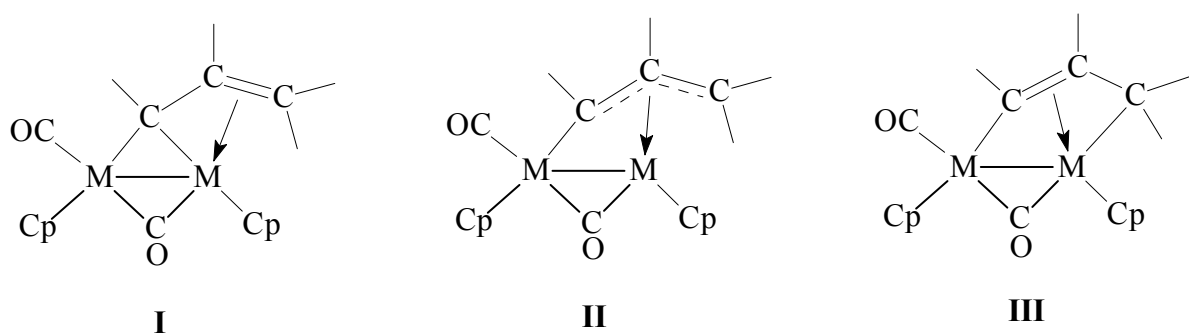
Complexes **6** and **8** are isomers, which could arise from either *cis-trans* arrangements of the Cp ligands or from axial and equatorial orientations of the C $_{\gamma}$ substituents. The former is the most likely on the basis of the IR and NMR data. *Cis* and *trans* isomers of complexes containing the [M $_2$ (Cp) $_2$ (CO) $_2$] unit (M = Fe, Ru) in several cases have distinctive frequencies for their higher carbonyl stretching vibration, the latter being at higher values in *cis* isomers than in the *trans* forms [13c-e, 20]. On this basis, a *cis* configuration is attributable to complex **8** and a *trans* configuration to complex **6**. This attribution is supported by comparing the ^1H NMR resonances of the Cp ligands of **6** and **8** with those of the *cis* and *trans* isomers of the parent complex **2b** [12], and by the order in which compounds **6** and **8** are eluted from the chromatographic column. Thus **6**, which is expected to be less polar than **8**, is eluted with a less polar solvent. Moreover, the C $_{\gamma}$ -Me resonances for **6** and **8**, in both the ^1H and ^{13}C NMR spectra, are very similar (*e.g.* in the ^1H NMR spectra: for **6**, δ 2.25 ppm; for **8**, δ 2.24 ppm), while the C $_{\alpha}$ resonances in the ^{13}C NMR spectra differ significantly (for **6**: δ = 113.5 ppm; for

8: $\delta = 118.1$ ppm). The opposite trends should be apparent if compounds **6** and **8** have different orientations of the methyl and phenyl groups at C_γ and the same arrangement of the Cp ligands. In **6** and **8** the C_γ substituents are expected to adopt the same orientations found in the precursor **2b**, where the hindered phenyl group points away from the Cp rings, lying in an axial position.

The structures shown in scheme 3, with bridging rather than terminal hydride, are as expected for compounds **6,8**. Hydrides are usually found acting as bridging ligands in diruthenium complexes [14a, 21], and examples of terminal coordination are rare [22]. IR spectroscopy is strongly diagnostic in determining which coordination is adopted by hydride in a dinuclear complex, since the band due to terminal Ru-H stretching is observable at *ca.* 1960 cm^{-1} [22a,c]. No such band is observed in the IR spectra of **6,8**.

Compound **9** (and its analogue **11**, see later) belongs to a large class of diruthenium and diiron complexes which have been reported in the literature. Such complexes consist of a *cis*- $[M_2(Cp)_2(CO)(\mu-CO)]$ core ($M = Ru, Fe$) and a bridging $\mu-\eta^1:\eta^3$ -vinylalkylidene ligand (scheme 5, structure I), which has been alternatively described as $\mu-\eta^1:\eta^3$ -allylidene (scheme 5, structure II) or 1,2-dimetalla-cyclo-pent-3-ene (scheme 5, structure III) [23].

Scheme 5



The spectroscopic characteristics of **9** are consistent with those of the analogous species. The IR spectrum (in CH_2Cl_2 solution) shows two bands at 1951 and 1774 cm^{-1} , accounting for terminal and bridging carbonyls, respectively. In the 1H NMR spectrum, which has a single set of resonances, the $C_\alpha-H$ proton resonates as a doublet ($J\ 7.2\text{ Hz}$), due to coupling with $C_\beta-H$, at the typically low field ($\delta\ 10.75\text{ ppm}$) expected for a proton bound to a bridging

alkylidene carbon; C_β-H is seen at δ 4.71 ppm. In the ¹³C NMR spectrum, the resonances of the C_α, C_β and C_γ carbons are found at δ 155.4, 82.7 and 71.1 ppm respectively. These values are consistent with the alkylidene character of C_α and with the olefin-bound-to-metal nature of C_β and C_γ.

2. Studies on the thermal stabilities of the products of the reaction of **3b** with NaBH₄

The IR spectrum of the mixture formed in the reaction of **3b** with NaBH₄ (see above) indicates that the mixture contains mainly compounds **6** and **8**, and suggests that the other products isolated by chromatography might derive from **6** and **8** through subsequent intramolecular rearrangements.

In order to investigate this possibility, solutions of complexes **5,6,8** and **9** were heated and monitored *via* IR spectroscopy. These studies have suggested a plausible mechanism for the formation of **6**, **5** and **9**, shown in scheme 6. Moreover, it has been possible to deduce a scale of thermodynamic stability, with the vinyl-alkylidene species **9** as the most stable product. This result is in accordance with previous findings, which indicate that μ-allenyl complexes undergo nucleophilic additions preferentially at the central carbon (C_β) of the C₃ chain [24], although examples of additions at C_α have also been reported [5a, 25].

Compound **8** is the main fraction collected by chromatography, in spite of the fact it is not stable in boiling n-heptane solution. This abundance is probably due to the following kinetic reasons: i) complex **8** results directly from **3b** by nitrile substitution with hydride; ii) the configuration of the Cp ligands (*cis*) is that presumably favoured in the parent cationic allenyl complexes [12]. In other words, the synthesis of **8** consists of simple substitution at the metal centres and would not require a rearrangement of the Cp rings.

Complex **8** undergoes clean and complete *cis*-to-*trans* isomerisation after 30 minutes in heptane at reflux temperature, to give **6**. *Cis-trans* isomerizations are common in dinuclear complexes of ruthenium and iron. Adams and Cotton proposed a mechanism for the *cis-trans* isomerization of [Fe₂(μ-CO)₂(CO)₂(Cp)₂] which is now a fundamental example of the dynamic behaviour of metal carbonyl compounds [26]. Moreover, *cis-trans* interconversion has been investigated in [Ru₂(μ-CO)₂(CO)₂(Cp)₂] [27] and related dinuclear complexes [21e, 28].

Compound **6** transforms cleanly, in boiling heptane over 7 hours, into the μ-η²:η² allene species **5b**. It is noteworthy that complex **5b** is obtained in the absence of **5a** under these

conditions, contrary to what was found after chromatography at low temperature. It may be concluded that **5b** is thermodynamically more stable than **5a**. Formation of **5a** in significant amounts at low temperature is probably because it has the same arrangement of the C_γ substituents as the allenyl precursor (see scheme 4). The rearrangement which leads from **6** to **5b** consists of hydride migration from the metal site to the C_α carbon of the allenyl moiety. It is probable that, both on the alumina column and in boiling heptane, compounds **5a,b** derive from **6** (and not from **8**) since this route does not require any modification of the arrangement of the Cp ligands.

Finally, if an n-heptane solution of **5b** is heated for 42 hours, formation of **9** occurs, accompanied by some decomposition, as a result of hydrogen migration from C_α to C_β, together with *trans*-to-*cis* isomerisation. Compound **9** is stable in boiling heptane solution upon further heating (7 hours).

Scheme 6

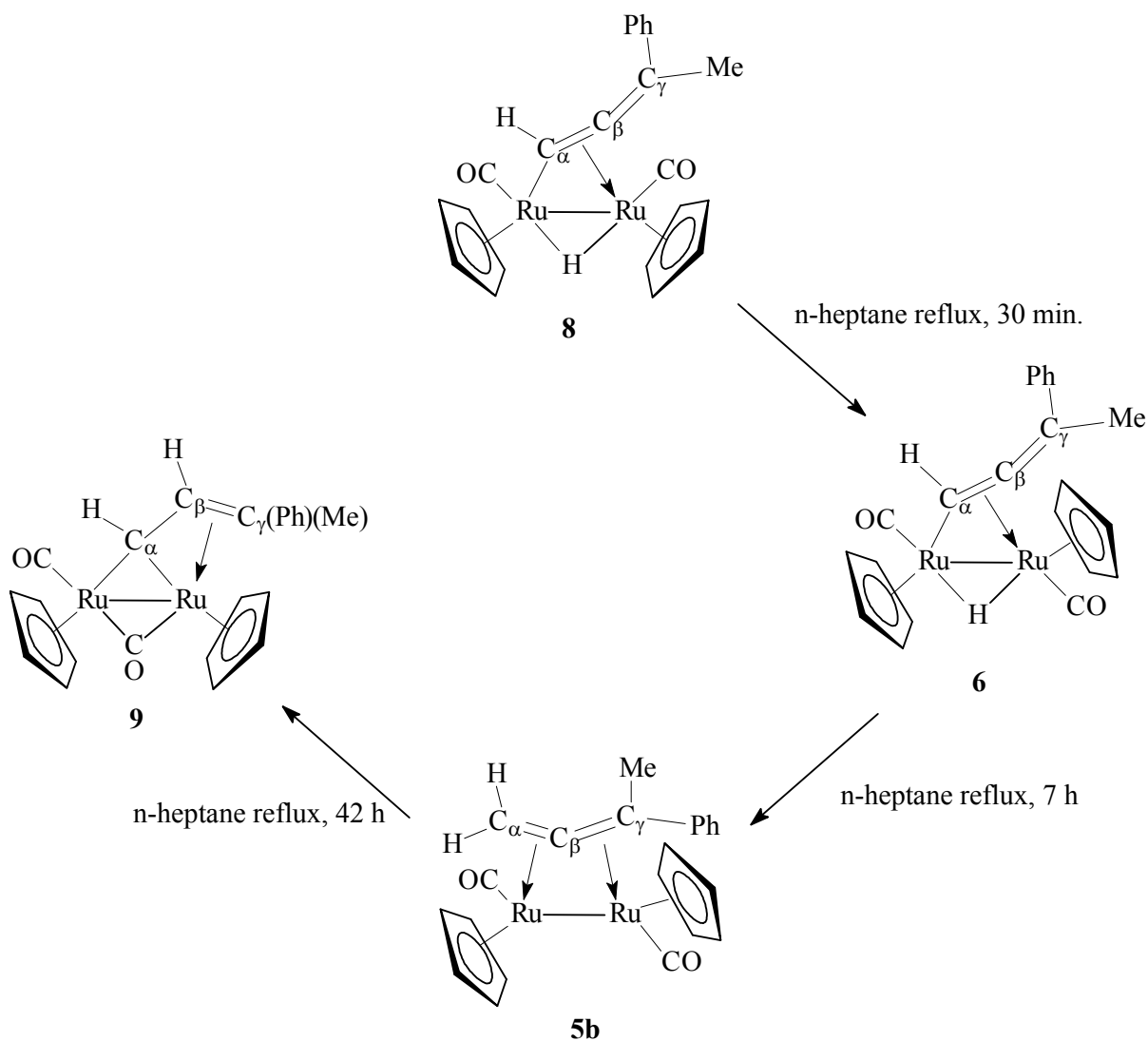


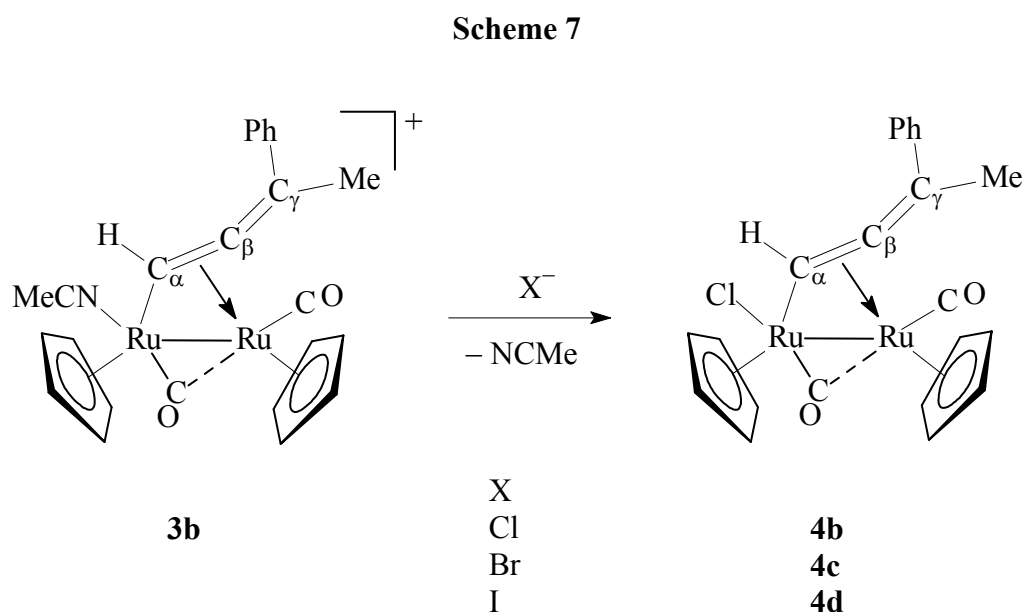
Table 1

Relevant ^1H NMR resonances for the compounds involved in the reactions shown in scheme 6.

Complex	8	6	5b	9
$\underline{\mu\text{-H}}$	-14.20	-13.73		
$\underline{\text{C}_\alpha\text{-H}}$	9.12	8.80	3.72, 2.85	10.75
$\underline{\text{C}_\beta\text{-H}}$				4.71

3. Reactivity of acetonitrile derivatives of diruthenium allenyl complexes with halides

The possibility of introducing simple anions at the metal sites of the diruthenium species **3**, and observing subsequent migration to the allenyl ligand, led us to investigate the reactivity of **3b** with halides. The reactions of **3b** with Cl^- (from LiCl), Br^- (from LiBr) and I^- (from KI) occur rapidly in the presence of a large excess of the salt in THF solution, to afford the neutral products $[\text{Ru}_2(\text{CO})_2(\text{X})\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C}_\alpha(\text{H})=\text{C}_\beta=\text{C}_\gamma(\text{Me})(\text{Ph})\}(\text{Cp})_2]$ [$\text{X} = \text{Cl}$, **4b**; $\text{X} = \text{Br}$, **4c**; $\text{X} = \text{I}$, **4d**] (scheme 7).

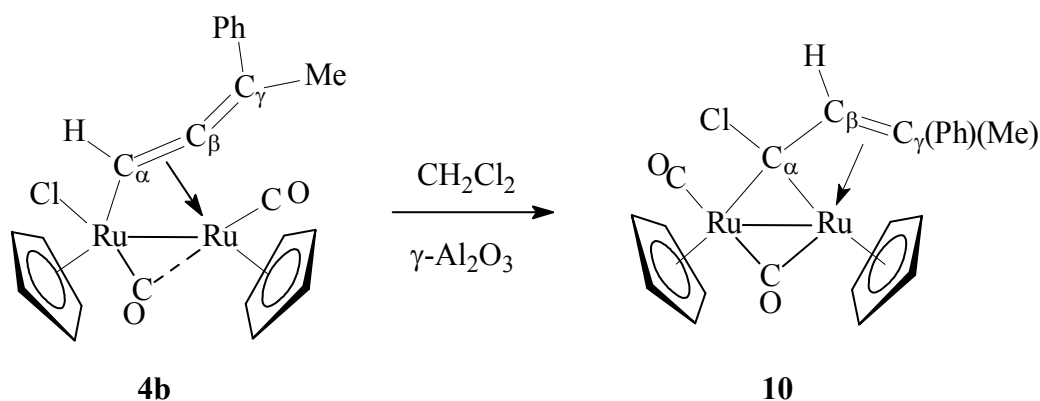


Compounds **4b-d** were purified by quick filtration through alumina and fully characterized by IR and NMR spectroscopy, elemental analysis and mass spectrometry. The molecular structures of **4b-d** are likely to resemble that determined in the solid state for $[\text{Ru}_2(\text{CO})_2(\text{Cl})\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C}(\text{H})=\text{C}=\text{C}(\text{Me})_2\}(\text{Cp})_2]$, **4a**; this latter complex, which has a *trans* geometry for the Cp rings, contains two carbonyls, one terminally bonded to one ruthenium atom, and one semi-bridging. The X ray structure of **4a** revealed that the allenyl ligand bridges the two ruthenium atoms in an identical fashion to that found for **2b** [12], with a σ bond to one metal and a π bond to the other. Moreover, the chloride ligand is bound to the ruthenium which is σ -bound to the allenyl.

The mono-halide species **4b-d** show very similar spectroscopic patterns, analogous to that of **4a**. The IR spectra (in CH_2Cl_2 solution) exhibit two bands at *ca.* 1985 and 1890 cm^{-1} , corresponding to one terminal and one semibridging carbonyl, respectively. The ^1H NMR

spectra of the compounds, recorded at room temperature, show the absence of fluxionality. Moreover, the NMR spectra of **4b** contain two sets of signals, in *ca.* 4:1 ratio. It is proposed that the two sets are due to *cis* and *trans* isomers, in agreement with what was reported for **4a**, although it is difficult to deduce which set of resonances is which. The salient ^1H and ^{13}C NMR features of **4b-d** do not significantly differ from the data available for **4a**, **2b**, **6** and **8**. Thus, a resonance at *ca.* 10 ppm is seen for the $\text{C}_\alpha\text{-H}$ proton, while the carbons of the allenyl chain resonate, for example in the case of **4d**, at δ 120.7 (C_α), 160.4 (C_β) and 113.7 (C_γ) ppm. Moreover, the resonances of the carbonyl ligands are found at *ca.* 202 and 213 ppm, in accord with the terminal and semi-bridging coordination modes, respectively, suggested by IR data. The substitution of one nitrile ligand by halides has been previously described for dinuclear complexes containing the unit $[\text{M}_2\text{Cp}_2(\text{CO})_2]$, $\text{M} = \text{Fe}, \text{Ru}$ [13b-e]. The reaction which leads to **4c** is accompanied by fragmentation, since small amounts (12 %) of the known monomer $[\text{Ru}(\text{Cp})(\text{CO})_2(\text{Br})]$ [29] were isolated upon chromatography. More interestingly, we have observed that compound **4b**, in dichloromethane solution, is not stable upon slow filtration through the alumina used for chromatographic separations. Thus, passing a CH_2Cl_2 solution of **4b** through an alumina column (see experimental) results in clean formation of an orange product which has been identified as $[\text{Ru}_2(\text{CO})(\mu\text{-CO})\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C}_\alpha(\text{Cl})\text{C}_\beta(\text{H})=\text{C}_\gamma(\text{Me})(\text{Ph})\}(\text{Cp})_2]$, **10**, an isomer of **4b** (scheme 8).

Scheme 8



Evidence for terminal and symmetrically bridging carbonyls in **10** is provided by IR absorptions at 1985 and 1832 cm^{-1} respectively. The ^1H NMR spectrum displays resonances for the phenyl protons (7.80-7.05 ppm), the olefinic $\text{C}_\beta\text{-H}$ (5.59 ppm), the Cp rings (5.26, 4.57 ppm), and the $\text{C}_\gamma\text{-Me}$ group (1.48 ppm), respectively. In particular, the absence of a low-field

signal, attributable to an alkylidene proton, suggests the modification of the allenyl moiety present in the starting compound **4b**. Unfortunately, complex **10** is not sufficiently soluble to record a satisfactory ^{13}C NMR spectrum, or to grow crystals suitable for X-ray analysis. However, elemental analysis for C, H and Cl, and the mass spectrum confirmed the identity of **10**.

According to the sequence shown in scheme 6, the bridging vinyl-chlorocarbene ligand of complex **10** might be the result of chloride migration from the metal to the C_α carbon of the allenyl ligand, followed by hydrogen migration from C_α to C_β . Nonetheless, attempts to convert **4b** into **10** upon heating in solution were unsuccessful: complex **4b** is unaltered after 15 hours in boiling toluene. This experimental evidence suggests that the possibility that complex **10** forms by a reaction of **4b** with CH_2Cl_2 on alumina, rather than by intramolecular rearrangements of **4b**, should not be excluded. Somewhat surprisingly, the transformation depicted in scheme 8 is limited to compound **4b**, since the analogous species **4a,4c-d** are stable upon passage through alumina. Terminal halocarbene ligands are well known species [30], however only a few cases of bridging halocarbenes have been reported, and they usually involve the CF_2 unit bridging between two metal centres [31]. Compound **10** contains the first example of a bridging vinyl-chlorocarbene ligand.

Conclusions

The substitution of a carbonyl ligand by an acetonitrile molecule in cationic diruthenium allenyl complexes allows the introduction of hydride and halide ions to the metal sites under mild conditions.

The resulting products undergo successive rearrangements which involve the bridging allenyl ligand. These can be promoted by: i) thermal treatment, ii) filtration through alumina, and iii) both. Hydride migration from the metal site to the C_α carbon of the allenyl moiety provides a $\mu\text{-}\eta^2\text{:}\eta^2$ allene adduct. The latter can be isolated and characterized, but it is further convertible into a more stable vinyl-alkylidene derivative, by hydrogen migration from C_α to C_β .

Likewise, an unprecedented example of a bridging vinyl-chlorocarbene species might be the result of chloride migration from the ruthenium centre to the C_α carbon of the allenyl ligand, occurring simultaneously with hydrogen migration from C_α to C_β .

Experimental Section

General Data. All reactions and general manipulations were carried out under a nitrogen atmosphere, using solvents dried by distillation from appropriate drying agents. Chromatographic separations were carried out on columns of deactivated alumina (6% w/w water), at $-35\text{ }^{\circ}\text{C}$. All reactions were monitored by IR spectroscopy. IR spectra were recorded on a Perkin-Elmer 1710 FT-IR spectrometer, using calcium fluoride cells of 1 mm path length. EI and FAB mass spectra were recorded on a Fisons Autospec instrument. Elemental analyses were performed by the Microanalytical laboratory of the School of Chemistry, University of Bristol. All NMR measurements were performed on JEOL GX 400 spectrometer, operating in Fourier transform mode. The chemical shifts for ^1H and ^{13}C were referenced to internal TMS. All the reagents were commercial products of the highest purity available and used as received, except for $[\text{Ru}_2(\text{CO})_2(\mu\text{-CO})\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C(H)=C=C(Me)(Ph)}\}(\text{Cp})_2][\text{BF}_4]$, **2b**, which was prepared according to the published method [12].

Synthesis of $[\text{Ru}_2(\text{CO})(\text{NCMe})(\mu\text{-CO})\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C(H)=C=C(Me)(Ph)}\}(\text{Cp})_2][\text{BF}_4]$, **3b.** Complex $[\text{Ru}_2(\text{CO})_2(\mu\text{-CO})\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C(H)=C=C(Me)(Ph)}\}(\text{Cp})_2][\text{BF}_4]$, **2b** (200 mg, 0.316 mmol), was dissolved in CH_2Cl_2 (20 mL) and treated with a solution of Me_3NO in MeCN (3.3 mL, 0.33 mmol). The mixture was stirred for 15 minutes. The solvent was then removed under reduced pressure, giving a brown residue. The IR spectrum of the residue, dissolved in CH_2Cl_2 , indicated clean formation of **3b** [$\nu(\text{CO})$ 2005 (vs), 1870 (s) cm^{-1}].

Reaction of $[\text{Ru}_2(\text{CO})_2(\text{NCMe})\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C(H)=C=C(Me)(R)}\}(\text{Cp})_2][\text{BF}_4]$, **3b, with NaBH_4 .** Complex $[\text{Ru}_2(\text{CO})(\mu\text{-CO})(\text{NCMe})\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C(H)=C=C(Me)(Ph)}\}(\text{Cp})_2][\text{BF}_4]$, **3b**, freshly prepared by reacting $[\text{Ru}_2(\text{CO})_2(\mu\text{-CO})\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C(H)=C=C(Me)(Ph)}\}(\text{Cp})_2][\text{BF}_4]$, **2b** (400 mg 0.633 mmol), with Me_3NO in MeCN solution, was dissolved in THF (30 mL) and treated with NaBH_4 (240 mg, 6.34 mmol). The mixture was stirred for 1 h, then the solvent was removed under reduced pressure. The resulting residue was introduced to an alumina column (15 x 2.5 cm) and chromatographed at $-35\text{ }^{\circ}\text{C}$. The following products were collected by using varying amounts of n-hexane and CH_2Cl_2 as eluent and isolated as powders upon removal of the solvent under vacuum.

$[\text{Ru}_2(\text{CO})_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_\alpha\text{H}_2\text{=C}_\beta\text{=C}_\gamma(\text{Me})(\text{Ph})\}(\text{Cp})_2]$, **5a-b** (eluent: hexane/ CH_2Cl_2 95:5; colour: pale yellow). Yield: 30 mg, 9.1 %. Anal. Calcd. for $\text{C}_{22}\text{H}_{20}\text{O}_2\text{Ru}_2$: C, 50.96; H, 3.89.

Found: C, 50.80; H, 4.00. FAB-MS: 520 m/z. IR (CH₂Cl₂) $\nu(\text{CO})$ 1933 (m, sh), 1915 (s) cm⁻¹. ¹H NMR (CD₂Cl₂, 298 K) **5a**: δ 7.72-6.63 (5 H, Ph); 5.04, 4.87 (s, 10 H, Cp); 3.52, 2.60 (d, ²J_{HH} = 4.0 Hz, 2 H, C _{α} H₂); 1.82 (s, 3 H, Me); **5b**: δ 7.72-6.63 (5 H, Ph); 4.65, 4.35 (s, 10 H, Cp); 3.72, 2.85 (d, ²J_{HH} = 4.3 Hz, 2 H, C _{α} H₂); 2.17 (s, 3 H, Me). **5a/5b** ratio 6:5. ¹³C{¹H} NMR (CD₂Cl₂, 298 K) **5a**: δ 210.1, 206.5 (CO); 189.9 (C _{β}); 149.7 (ipso-Ph); 128.5, 127.7, 126.4 (Ph); 88.0, 86.1 (Cp); 62.1 (C _{γ}); 28.8 (Me); 25.0 (C _{α}); **5b**: δ 208.0, 207.1 (CO); 187.8 (C _{β}); 150.7 (ipso-Ph); 127.7, 125.4, 124.5 (Ph); 87.3, 84.0 (Cp); 56.9 (C _{γ}); 31.3 (Me); 29.7 (C _{α}).

trans-[Ru₂(CO)₂(μ -H){ μ - η^1 : η^2 -C _{α} H=C _{β} =C _{γ} (Me)(Ph)}(Cp)₂], **6** (eluent: hexane/CH₂Cl₂ 90:10; colour: yellow). Yield: 50 mg, 15 %. Anal. Calcd. for C₂₂H₂₀O₂Ru₂: C, 50.96; H, 3.89. Found: C, 50.79; H, 3.95. FAB-MS: 520 m/z. IR (CH₂Cl₂) $\nu(\text{CO})$ 1972 (m), 1918 (s) cm⁻¹. ¹H NMR (CD₂Cl₂, 298 K) δ 8.80 (q, ⁵J_{HH} = 2.5 Hz, 1 H, C _{α} H); 8.43-6.98 (5 H, Ph); 5.16, 4.76 (s, 10 H, Cp); 2.25 (d, ⁵J_{HH} = 2.5 Hz, 3 H, Me); -13.73 (s, 1 H, μ -H). ¹³C{¹H} NMR (CD₂Cl₂, 298 K) δ 203.1, 202.4 (CO); 162.7 (C _{β}); 140.1 (ipso-Ph); 128.4, 126.4, 125.0 (Ph); 113.5 (C _{α}); 110.9 (C _{γ}); 85.2, 85.0 (Cp); 22.2 (Me).

[Ru₃(CO)₃(μ -H)₃(Cp)₃], **7** (eluent: hexane/CH₂Cl₂ 90:10; colour: blue). Yield: 39 mg, 7.0 % [15].

cis-[Ru₂(CO)₂(μ -H){ μ - η^1 : η^2 -C _{α} H=C _{β} =C _{γ} (Me)(Ph)}(Cp)₂], **8** (eluent: hexane/CH₂Cl₂ 80:20; colour: yellow). Yield: 117 mg, 36 %. Anal. Calcd. for C₂₂H₂₀O₂Ru₂: C, 50.96; H, 3.89. Found: C, 51.10; H, 3.77. FAB-MS: 520 m/z. IR (CH₂Cl₂) $\nu(\text{CO})$ 1984 (vs), 1921 (s) cm⁻¹. ¹H NMR (CD₂Cl₂, 298 K) δ 9.12 (q, ⁵J_{HH} = 2.5 Hz, 1 H, C _{α} H); 7.81-6.57 (5 H, Ph); 5.14, 5.06 (s, 10 H, Cp); 2.24 (d, ⁵J_{HH} = 2.5 Hz, 3 H, Me); -14.20 (s, 1 H, μ -H). ¹³C{¹H} NMR (CD₂Cl₂, 298 K) δ 202.6, 201.7 (CO); 162.7 (C _{β}); 141.1 (ipso-Ph); 128.2, 126.5, 125.0 (Ph); 118.1 (C _{α}); 112.3 (C _{γ}); 84.7, 84.1 (Cp); 22.3 (Me).

[Ru₂(CO)(μ -CO){ μ - η^1 : η^3 -C _{α} (H)C _{β} (H)=C _{γ} (Me)(Ph)}(Cp)₂], **9** (eluent: hexane/CH₂Cl₂ 80:20; colour: yellow). Yield: 37 mg, 11 %. Anal. Calcd. for C₂₂H₂₀O₂Ru₂: C, 50.96; H, 3.89. Found: C, 51.14; H, 3.79. FAB-MS: 520 m/z. IR (CH₂Cl₂) $\nu(\text{CO})$ 1951 (vs), 1774 (s) cm⁻¹. ¹H NMR (CD₂Cl₂, 298 K) δ 10.75 (d, ³J_{HH} = 7.2 Hz, 1 H, C _{α} H); 7.58-6.50 (5 H, Ph); 5.08, 4.88 (s, 10 H, Cp); 4.71 (d, ³J_{HH} = 7.2 Hz, 1 H, C _{β} H); 1.59 (s, 3 H, Me). ¹³C{¹H} NMR (CD₂Cl₂, 298 K) δ 239.4 (μ -CO); 200.5 (CO); 155.4 (C _{α}); 146.8 (ipso-Ph); 128.0, 127.7, 125.6 (Ph); 88.6, 85.7 (Cp); 82.7 (C _{β}); 71.1 (C _{γ}); 38.9 (Me).

Studies on the thermal stabilities of 5, 6, 8 and 9. Complex **8** (150 mg, 0.289 mmol) was dissolved in n-heptane (15 mL) and the solution was heated at reflux temperature for 30 minutes. The solution was then cooled to room temperature and the solvent was removed under vacuum, giving a yellow powder. IR and NMR spectroscopic data indicated complete conversion into complex **6**. The latter was purified by filtration on alumina. Yield: 130 mg, 87 %. The residue was then dissolved in n-heptane (15 mL), and heated at reflux temperature for 7 hours. The solution was then cooled and powdery **5b** was cleanly obtained upon removal of the solvent. The identity of **5b** was established by IR and ^1H NMR spectroscopy. Yield: 120 mg, 80 %. The yellow complex was dissolved in n-heptane (15 mL) and heated at reflux. IR spectroscopy revealed progressive formation of **9** and consumption of **5b**, which was completed after 42 hours. The final mixture was chromatographed on an alumina column and a yellow band was collected by using a mixture of CH_2Cl_2 and n-hexane (1:1 v:v) as eluent. Removal of the solvent gave a yellow powder, which was identified as complex **9** by IR and ^1H NMR spectroscopy. Yield: 79 mg, 53 %. Finally, a solution of complex **9** was boiled in n-heptane (10 mL) for 7 hours, but no variation was detected *via* IR.

Synthesis of $[\text{Ru}_2(\text{CO})_2(\text{X})\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C}_\alpha(\text{H})\text{=C}_\beta\text{=C}_\gamma(\text{Me})(\text{Ph})\}(\text{Cp})_2]$ [X** = Cl, **4b**; **X** = Br, **4c**; **X** = I, **4d**].** To a THF solution (20 mL) of complex $[\text{Ru}_2(\text{CO})(\text{NCMe})(\mu\text{-CO})\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C(H)=C=C(Me)(Ph)}\}(\text{Cp})_2][\text{BF}_4]$, **3b**, freshly prepared from $[\text{Ru}_2(\text{CO})_2(\mu\text{-CO})\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C(H)=C=C(Me)(Ph)}\}(\text{Cp})_2][\text{BF}_4]$, **2b** (200 mg 0.316 mmol), LiCl (260 mg, 6.13 mmol) was added. The resulting mixture was stirred for 1 h, then it was introduced to a short alumina column (3 x 2.5 cm). Quick filtration with a mixture of THF and methanol (95:5 v:v) afforded an orange solution of **4b**, which gave an ochre yellow powder upon removal of the solvent under reduced pressure. Yield: 133 mg, 76 %. Anal. Calcd. for $\text{C}_{22}\text{H}_{19}\text{ClO}_2\text{Ru}_2$: C, 47.78; H, 3.46; Cl, 6.41. Found: C, 47.65; H, 3.23; Cl, 6.19. EI-MS: 554 m/z. IR (CH_2Cl_2) $\nu(\text{CO})$ 1989 (vs), 1887 (s) cm^{-1} . ^1H NMR (CDCl_3 , 298 K) Major isomer: δ 9.80 (q, $^5J_{\text{HH}} = 1.9$ Hz, 1 H, C_αH); 7.77-7.24 (5 H, Ph); 5.30, 4.78 (s, 10 H, Cp); 2.28 (d, $^5J_{\text{HH}} = 1.9$ Hz, 3 H, Me); Minor isomer: δ 9.87 (q, $^5J_{\text{HH}} = 1.9$ Hz, 1 H, C_αH); 7.77-7.24 (5 H, Ph); 5.21, 4.84 (s, 10 H, Cp); 1.92 (d, $^5J_{\text{HH}} = 1.9$ Hz, 3 H, Me). *Isomer ratio* 4:1. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 298 K) δ 213.0 (s-CO); 201.0 (CO); 158.4 (C_β); 138.6 (ipso-Ph); 130.5 (C_α); 128.3, 126.2 (Ph); 114.6 (C_γ); 88.3, 86.1 (Cp); 22.6 (Me).

Compounds **4c-d** were prepared by the same procedure described for **4b**, by reacting **3b** with the appropriate halide salt (LiBr, KI).

4c (yield: 85 %; colour: orange). Anal. Calcd. for C₂₂H₁₉BrO₂Ru₂: C, 44.23; H, 3.21; Br, 13.37. Found: C, 44.35; H, 3.15; Br, 13.12. FAB-MS: 598 m/z. IR (CH₂Cl₂) ν (CO) 1986 (vs), 1890 (s) cm⁻¹. ¹H NMR (d⁸-toluene, 298 K) δ 9.80 (q, ⁵J_{HH} = 2.0 Hz, 1 H, C _{α} H); 7.70-7.19 (5 H, Ph); 4.80, 4.60 (s, 10 H, Cp); 2.02 (d, ⁵J_{HH} = 2.0 Hz, 3 H, Me). ¹³C{¹H} NMR (d⁸-toluene, 298 K) δ 210.5 (s-CO); 201.9 (CO); 160.1 (C _{β}); 138.9 (ipso-Ph); 129.0 (C _{α}); 128.1, 127.9, 126.0 (Ph); 113.9 (C _{γ}); 88.1, 86.4 (Cp); 29.0 (Me).

4d (yield: 89 %; colour: orange). Anal. Calcd. for C₂₂H₁₉IO₂Ru₂: C, 41.00; H, 2.97; I, 19.69. Found: C, 41.09; H, 3.06; I, 19.84. FAB-MS: 646 m/z. IR (CH₂Cl₂) ν (CO) 1984 (vs), 1891 (s) cm⁻¹. ¹H NMR (d⁸-toluene, 298 K) δ 9.82 (q, ⁵J_{HH} = 2.2 Hz, 1 H, C _{α} H); 7.54-6.63 (5 H, Ph); 4.47, 4.28 (s, 10 H, Cp); 1.97 (d, ⁵J_{HH} = 2.2 Hz, 3 H, Me). ¹³C{¹H} NMR (d⁸-toluene, 298 K) δ 209.2 (s-CO); 202.9 (CO); 160.4 (C _{β}); 140.0 (ipso-Ph); 128.6, 126.5, 126.1 (Ph); 120.7 (C _{α}); 113.7 (C _{γ}); 88.2, 86.9 (Cp); 30.4 (Me).

Synthesis of [Ru₂(CO)(μ -CO){ μ - η^1 : η^3 -C _{α} (Cl)C _{β} (H)=C _{γ} (Me)(Ph)}(Cp)₂], **10.** Complex [Ru₂(CO)₂(Cl){ μ - η^1 : η^2 -C(H)=C=C(Me)(Ph)}(Cp)₂], **4b** (120 mg, 0.217 mmol), was dissolved in dichloromethane (15 mL) and introduced to an alumina column (15 x 2.5 cm). An orange band corresponding to **10** was collected by using neat CH₂Cl₂ as eluent. Compound **10** was obtained as an air stable orange powder upon removal of the solvent under reduced pressure. Yield: 85 mg, 71 %. Anal. Calcd. for C₂₂H₁₉ClO₂Ru₂: C, 47.78; H, 3.46; Cl, 6.41. Found: C, 47.62; H, 3.29; Cl, 6.30. EI-MS: 554 [M⁺], 526 [M⁺ - CO], 519 [M⁺ - Cl] m/z. IR (CH₂Cl₂) ν (CO) 1985 (vs), 1832 (s) cm⁻¹. ¹H NMR (CD₂Cl₂, 298 K) δ 7.80-7.05 (5 H, Ph); 5.59 (s, 1 H, C _{β} H); 5.26, 4.57 (s, 10 H, Cp); 1.48 (s, 3 H, Me).

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