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Synthesis and reactivity of dimetallacyclopentenone complexes $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)CR^1CR^2\}(\eta\text{-}C_5H_5)_2]$ (R^1 = Me or Ph; $R^2 = CO_2Me$)

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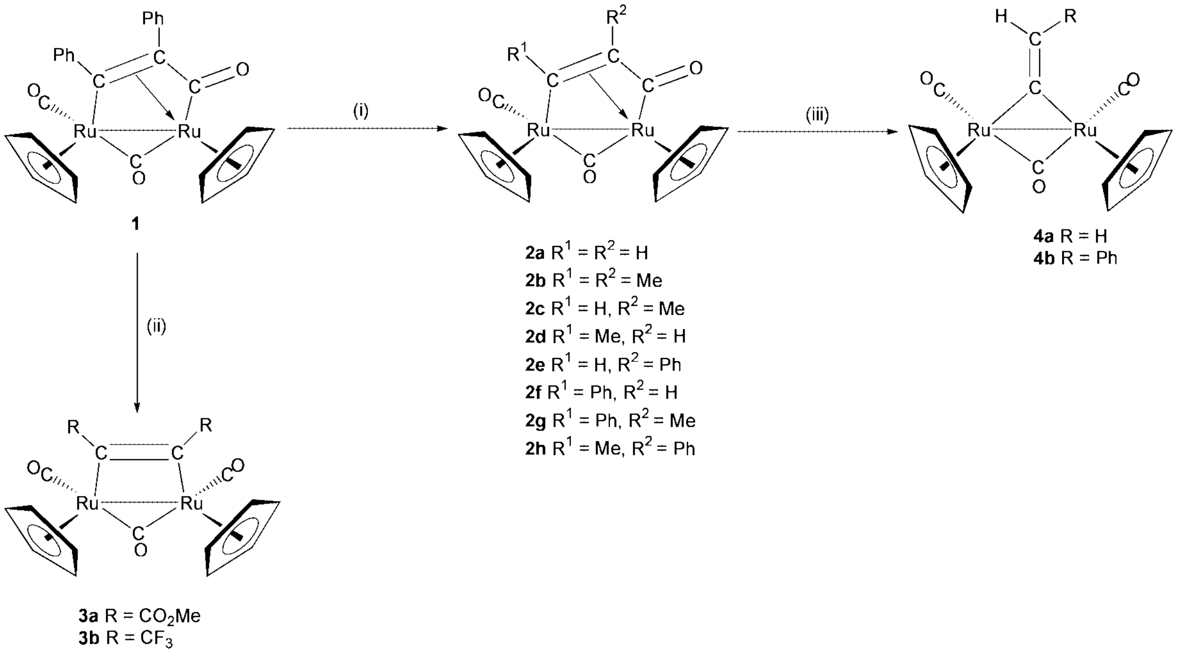
Received 19th April 2000, Accepted 4th July 2000

Reactions of the dimetallacyclopentenone complex $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}(\eta\text{-}C_5H_5)_2]$ (**1**) with alkynes $RC{\equiv}CCO_2Me$ (R = Me or Ph) lead to alkyne exchange, forming inseparable isomeric mixtures of $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C(R)C(CO_2Me)\}(\eta\text{-}C_5H_5)_2]$ and $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C(CO_2Me)C(R)\}(\eta\text{-}C_5H_5)_2]$ (**2i**,**j**, R = Ph; **2k**,**l**, R = Me), whereas with $HC{\equiv}CCO_2Me$ the μ-vinylidene complex $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C{=}C(H)CO_2Me\}(\eta\text{-}C_5H_5)_2]$ (**4c**) is produced. The new dimetallacyclopentenone complexes undergo fluxional processes which interconvert the isomers with free energies of activation similar to those seen previously for other diruthenacyclopentenone species. Both **2i**,**j** and **2k**,**l** are thermally stable but UV irradiation of **2i**,**j** yields $[Ru_2(\mu\text{-}CO)\{\mu\text{-}\eta^2{:}\eta^2\text{-}C(Ph)C(CO_2Me)\}(\eta\text{-}C_5H_5)_2]$ (**5**), $[Ru_2(CO)_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}C(O)C_6H_4C{=}C(H)CO_2Me)\}(\eta\text{-}C_5H_5)_2]$ (**6**) and $[Ru_3(CO)(\mu\text{-}CO)_2\{\mu_3\text{-}\eta^2\text{-}C(Ph)C(CO_2Me)\}(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)(\eta\text{-}C_5H_5)_2]$ (**7**), while photolysis of **2k**,**l** generates the μ-allylidene complex $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(CO_2Me)CH{=}CH_2\}(\eta\text{-}C_5H_5)_2]$ (**8**). The structures of the unusual complexes **6** and **7** have been determined by X-ray diffraction studies. Complexes **5**, **6** and **7** are shown to be formed from **2i**,**j** *via* independent pathways.

Introduction

We have previously reported that the dimetallacyclopentenone complex $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}(\eta\text{-}C_5H_5)_2]$ (**1**) undergoes thermally induced exchange reactions with alkynes to give analogous dimetallacyclopentenones **2a**–**h** or dimetallacyclobutene complexes **3a**,**b**, and that heating dimetallacyclopentenones derived from alkynes $RC{\equiv}CH$ (R = H, Ph) induces a proton shift to give μ-vinylidene complexes **4a**,**b** (see Scheme 1).[1–3] It is clear that the nature of the alkyne substituents is critical in determining the pathway followed and that electron withdrawing groups strongly favour the formation of dimetallacyclobutene complexes, either because they stabilise the metal–carbon σ-bonding in these species or, more likely, because they would make the ethylenic double bond in a dimetallacyclopentenone a poor donor.

This paper describes an extension of these studies: an investigation of the reactivity of complex **1** towards a series of alkynes $RC{\equiv}CCO_2Me$ (R = H, Me, Ph), designed to determine the effect of having only one strongly electron-withdrawing substituent. It shows (a) that this is insufficient to direct the reaction towards a dimetallacyclobutene, *i.e.* the products are of type **2** for R = Me or Ph, (b) that it induces direct formation of a μ-vinylidene species **4** when R = H, and (c) that



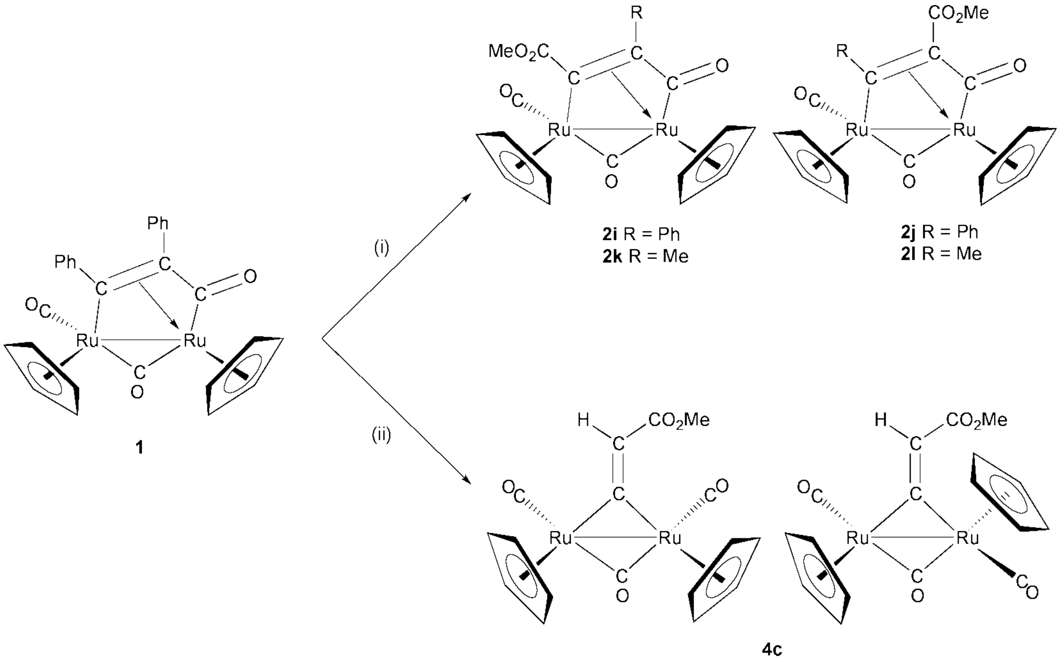
Scheme 1 (i) $R^1C_2R^2$, toluene, reflux; (ii) RC_2R, toluene reflux; (iii) **2a** and **2e**,**f**, toluene reflux.

DOI: 10.1039/b003156i

Table 1 Analytical and physical data for new complexes

Complex		Colour	M[a,d]	Analysis[a,b] (%)	
				C	H
$[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2(Ph)(CO_2Me)\}(\eta\text{-}C_5H_5)_2]$	**2i,j**	Orange	578(578)	48.15(47.76)	3.05(3.14)
$[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2(Me)(CO_2Me)\}(\mu\text{-}C_5H_5)_2]$	**2k,l**	Orange	515(515)	42.52(42.02)	3.12(3.14)
trans-$[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C{=}C(H)CO_2Me\}(\mu\text{-}C_5H_5)_2]$	*trans*-**4c**	Yellow	501(501)	40.68(40.65)	2.85(2.81)
cis-$[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C{=}C(H)CO_2Me\}(\mu\text{-}C_5H_5)_2]$	*cis*-**4c**	Yellow	501(501)	41.05(40.65)	2.82(2.81)
$[Ru_2(\mu\text{-}CO)\{\mu\text{-}C(Ph)C(CO_2Me)\}(\mu\text{-}C_5H_5)_2]$	**5**	Green	522(522)	49.12(48.46)[c]	3.70(3.49)
$[Ru_2(CO)_2\{\mu\text{-}C(O)C_6H_4C{=}C(H)CO_2Me\}(\mu\text{-}C_5H_5)_2]$	**6**	Orange	578(578)	48.02(47.92)	3.40(3.15)
$[Ru_3(CO)(\mu\text{-}CO)_2\{\mu_3\text{-}C(Ph)C(CO_2Me)\}(\mu\text{-}C_5H_4)(\mu\text{-}C_5H_5)_2]$	**7**	Red	745(745)[e]	45.49(45.34)[c]	3.08(2.99)
$[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(CO_2Me)C(H){=}CH_2\}(\mu\text{-}C_5H_5)_2]$	**8**	Orange	487(487)	42.19(41.81)	3.30(3.31)

[a] Calculated values in parentheses. [b] Recrystallised from dichloromethane–hexane unless otherwise stated. [c] Recrystallised from toluene–hexane. [d] By mass spectrometry with electron-impact ionisation. [e] By mass spectrometry with fast atom bombardment ionisation.



Scheme 2 (i) RC_2CO_2Me, toluene reflux; (ii) HC_2CO_2Me, toluene reflux.

the new dimetallacyclopentenones, unlike previously obtained analogues, undergo photolysis to give products with unprecedented structures.

Results and discussion

Alkyne exchange reactions

UV irradiation of a toluene solution of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and the alkynes $RC{\equiv}CCO_2Me$ (R = H, Me, Ph), followed by chromatography, led only to retrieval of starting material and several low yield oily products which could not be characterised. These results are in accord with our previous observation[1] that only diphenylacetylene reacts with $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ to give an isolable product, the dimetallacyclopentenone species **1**. However, complex **1** reacts with other alkynes in exchange processes and a similar situation exists with $RC{\equiv}CCO_2Me$, as shown in Scheme 2.

Heating a toluene solution of **1** and methyl phenylpropiolate at reflux for 10 min afforded an inseparable mixture of the isomeric dimetallacyclopentenones $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C(Ph)C(CO_2Me)\}(\eta\text{-}C_5H_5)_2]$ (**2i**) and $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C(CO_2Me)C(Ph)\}(\eta\text{-}C_5H_5)_2]$ (**2j**) in 73% yield. Similarly, reaction of **1** with methyl 2-butynoate yielded a mixture of the isomers $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C(Me)C(CO_2Me)\}(\eta\text{-}C_5H_5)_2]$ (**2k**) and $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C(CO_2Me)C(Me)\}(\eta\text{-}C_5H_5)_2]$ (**2l**) in 60% yield. Analytical and spectroscopic data for the new complexes are consistent with their formulation and are given in Tables 1 and 2.

Proton NMR spectra of **2i,j** and **2k,l** show that the isomers are present in 5 : 4 and 7 : 1 ratios respectively in dichloromethane solution at room temperature. Assignment of the structures **2k** and **2l** as the major and minor isomers respectively is readily achieved by comparing their methyl group signals with those of **2c,d** and **2g,h**.[1] Thus, a high field signal at δ 1.69 is consistent with a methyl group attached to an olefinic carbon, *i.e.* **2k**, while a lower field resonance at δ 2.81 is in accord with a methyl group on the bridging carbon, *i.e.* **2l**. This assignment is also in accord with previous observations that for asymmetrically substituted dimetallacyclopentenones the favoured isomer is that with the most electron withdrawing substituent on the bridging carbon.[1] This leads us to propose that for **2i,j** the major isomer is **2i** and the minor one is **2j**; the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra do not clearly distinguish the isomers. The isomeric ratios of 7 : 1 for **2k,l** and 5 : 4 for **2i,j** reflect the greater difference in the electron withdrawing properties of the CO_2Me and Me groups compared to the CO_2Me and Ph groups.

In an attempt to produce a dimetallacyclobutene complex of type **3** the reaction of **1** with the alkynes was carried out for longer times but this had no effect on the nature of the products; after 4 h only lower yields of the dimetallacycles **2i,j** and **2k,l** were obtained and decomposition was observed. Heating toluene solutions of pure **2i,j** or **2k,l** also resulted in some

Table 2 IR and NMR data for new complexes

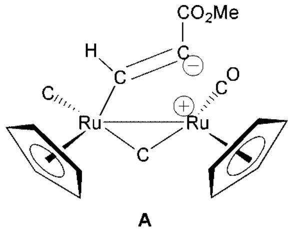
Complex	ν_{CO}[a] cm^{-1}	^{1}H NMR[b,c] (δ)	^{13}C-{^{1}H} NMR[b] (δ)
2i	1999s, 1812m, 1752w, 1770w	7.34–7.11 (m, 5H), 5.41 (s, 5H), 5.12 (s, 5H), 3.51 (s, 3H).	233.7 (μ-CO), 216.0 (C=O), 199.5 (CO), 176.2 (*C*O$_2$Me), 135.6 (μ-*C*CO$_2$Me), 134.6 (Ph), 128.8, 127.9, 125.3 (all Ph), 9.19 (C$_5$H$_5$), 91.2 (C$_5$H$_5$), 52.1 (CO$_2$*Me*), 43.4 (*C*Ph).
2j		7.34–7.11 (m, 5H), 5.34 (s, 5H), 5.23 (s, 5H), 3.71 (s, 3H).	238.0 (μ-CO), 216.0 (C=O), 199.2 (CO), 170.1 (*C*O$_2$Me), 160.0 (μ-*C*Ph), 149.6 (Ph), 128.4, 126.7 (all Ph), 90.6 (C$_5$H$_5$), 90.0 (C$_5$H$_5$), 52.4 (CO$_2$*Me*), 29.9 (*C*CO$_2$Me).
2k	1982s, 1810m, 1754w, 1707w	5.26 (s, 5H), 5.21 (s, 5H), 3.92 (s, 3H), 1.69 (s, 3H)[d]	234.0 (μ-CO), 218.9 (C=O), 198.9 (CO), 176.0 (*C*O$_2$Me), 160.8 (μ-*C*CO$_2$Me), 90.1 (C$_5$H$_5$), 89.3 (C$_5$H$_5$), 52.1 (CO$_2$*Me*), 39.1 (*C*Me), 17.4 (Me).[d]
2l		5.33 (s, 5H), 5.30 (s, 5H), 3.74 (s, 3H), 2.81 (s, 3H)	91.2 (C$_5$H$_5$), 91.0 (C$_5$H$_5$).[e]
trans-**4c**	1967s, 1801s, 1703m	7.19 (s, 1H), 5.32 (s, 5H), 5.22 (s, 5H), 3.65 (s, 3H).[d]	275.8 (μ-C), 241.3 (μ-CO), 197.4 (CO), 197.3 (CO), 164.6 (*C*O$_2$Me), 129.6 (*C*(H)CO$_2$Me), 92.7 (C$_5$H$_5$), 92.3 (C$_5$H$_5$), 50.6 (CO$_2$*Me*).[d]
cis-**4c**	2004s, 1967s, 1801s, 1703m	7.13 (s, 1H), 5.28 (s, 5H), 5.20 (s, 5H), 3.64 (s, 3H).[d]	275.1 (μ-C), 242.2 (μ-CO), 197.8 (CO), 197.7 (CO), 164.6 (*C*O$_2$Me), 129.1 (*C*(H)CO$_2$Me), 90.8 (C$_5$H$_5$), 90.0 (C$_5$H$_5$), 50.6 (CO$_2$*Me*).[d]
5	1759s, 1693m	7.35 (m, 5H), 4.92 (s, 10H), 3.81 (s, 3H).	175.2 (*C*O$_2$Me), 146.7 (μ-*C*Ph), 144.1 (Ph), 128.7, 128.4, 128.2 (all Ph), 121.8 (μ-*C*CO$_2$Me), 83.6 (2C$_5$H$_4$), 52.4 (CO$_2$*Me*).
6	1967s, 1936s, 1718m, 1626m	7.44–7.17 (m, 4H), 5.95 (s, 1H), 5.26 (s, 5H), 4.71 (s, 5H), 3.70 (s, 3H).	240.0 (C=O), 207.6 (CO), 204.5 (CO), 176.2 (μ-*C*), 175.1 (*C*O$_2$Me), 164.9 (*C*C=O), 150.2 (*C*C=C(H)-CO$_2$Me), 131.3, 128.6, 120.6, 117.3 (all CH), 90.6 (C$_5$H$_5$), 90.0 (C$_5$H$_5$), 51.6 (*C*(H)CO$_2$Me), 51.3 229.1 (μ-CO), 224.5 (μ-CO), 201.0 (CO), 179.6 (μ-*C*PH), (CO$_2$*Me*).
7	1971s, 1839s, 1799m, 1697m	7.22–7.06 (m, 5H), 5.63 (m, 1H), 5.35 (m, 1H), 5.23 (m, 1H), 5.00 (s, 5H), 4.94 (s, 5H), 4.66 (m, 1H), 3.65 (s, 3H).	179.5 (μ-*C*CO$_2$Me), 177.3 (*C*O$_2$Me), 154.2 (Ph), 127.6, 127.4, 125.6 (all Ph), 118.5 (C$_5$H$_4$), 109.5 (C$_5$H$_4$), 95.4 (C$_5$H$_4$), 92.0 (C$_4$H$_4$), 90.4 (C$_5$H$_5$), 88.6 (C$_5$H$_5$), 84.1 (C$_5$H$_4$), 51.2 (CO$_2$*Me*).
8	1952s, 1786s, 1699m	5.18 (s, 5H), 4.96 (s, 5H), 4.87 (dd, *J* 7, 9, 1H^a), 3.81 (s, 3H), 2.65 (dd, *J* 3, 7, 1H^b), −0.11 (dd, *J* 3, 9, 1H^c).	238.2 (μ-CO), 203.7 (CO), 179.7 (*C*O$_2$Me), 156.1 (μ-*C*), 89.4 (C$_5$H$_5$), 85.1 (C$_5$H$_5$), 80.7 (CH), 51.9 (CO$_2$*Me*), 40.6 (CH$_2$).

[a] Dichloromethane solution. [b] CD$_2$Cl$_2$ solution unless otherwise stated. [c] Coupling constant, *J*, in Hz. [d] CDCl$_3$ solution. [e] Minor isomer, other peaks not observed.

decomposition over several hours and again no dimetallacyclobutene complex was detected. It is evident, therefore, that the formation of a dimetallacyclobutene in this system requires the presence of two strongly electron withdrawing groups on the alkyne: a CO$_2$Me and a phenyl group are insufficient.

Heating a toluene solution of **1** with an excess of methyl propiolate for 4 h, followed by chromatography, led to the isolation of the yellow μ-vinylidene complex [Ru$_2$(CO)$_2$(μ-CO){μ-C=C(H)CO$_2$Me}(η-C$_5$H$_5$)$_2$] (**4c**) as *cis* and *trans* isomers in yields of 48 and 8% respectively. Characterisation of these complexes proved straightforward, by comparing their spectroscopic data with those of the isomers of the known complexes [Ru$_2$(CO)$_2$(μ-CO){μ-C=C(H)R}(η-C$_5$H$_5$)$_2$] (**4a**,**b**).[2] The *cis* and *trans* isomers can be distinguished by their IR spectra, that of the *cis* isomer showing two terminal carbonyl stretches at 2004 and 1967 cm^{-1}, whereas the more symmetric *trans* isomer displays just one terminal carbonyl band at 1967 cm^{-1}.

It has previously been observed that prolonged heating of the dimetallacyclopentenone species [Ru$_2$(CO)(μ-CO){μ-C(O)-C(H)C(R)}(η-C$_5$H$_5$)$_2$] (**2a**, R = H; **2e**,**f**, R = Ph) leads to formation of the corresponding vinylidene complexes **4a** and **4b**.[2] It is therefore likely that the reaction of **1** with methyl propiolate initially produces a dimetallacyclopentenone complex [Ru$_2$(CO)(μ-CO){μ-C(O)C(H)C(CO$_2$Me)}(η-C$_5$H$_5$)$_2$] which, under the reaction conditions, rapidly isomerises to the μ-vinylidene species **4c**. This is clear evidence that a strongly electron withdrawing substituent such as CO$_2$Me promotes the proton shift rearrangement of a dimetallacyclopentenone to give a vinylidene, a conclusion supported by the failure of the species **2c**,**d**, which have an electron donating methyl substituent, to undergo the rearrangement. This in turn suggests that the process may involve a charge-separated intermediate such as **A**, the negative charge of which would be stabilised by the CO$_2$Me group.



A

Fluxionality

We have previously shown[1] that dimetallacyclopentenone complexes undergo the fluxional process shown in Fig. 1, involving cleavage of the bond between C^2 and C^b with simultaneous formation of a new bond between C^1 and C^a. In effect the alkyne 'slides' back and forth between the C^{a}O and C^{b}O carbonyls. The ^{1}H NMR spectra of **2i**,**j** and **2k**,**l** reveal that these compexes are similarly fluxional. Thus, at room temperature the ^{1}H NMR spectrum of **2k**,**l** shows the four cyclopentadienyl signals and two methyl carboxylate signals expected of two static isomers, but as the temperature is raised the signals broaden and collapse, until coalescence occurs: at *ca.* 55 °C for the cyclopentadienyl signals and *ca.* 65 °C for the CO$_2$Me signals. On further warming the signals sharpen and at 80 °C two signals are observed for the cyclopentadienyl ligands and one for the CO$_2$Me groups, indicating rapid interconversion of the two isomers on the NMR timescale. Similar behaviour is seen for **2i**,**j** with the four cyclopentadienyl signals at room temperature undergoing coalescence at 60 °C and appearing as two signals at higher temperature.

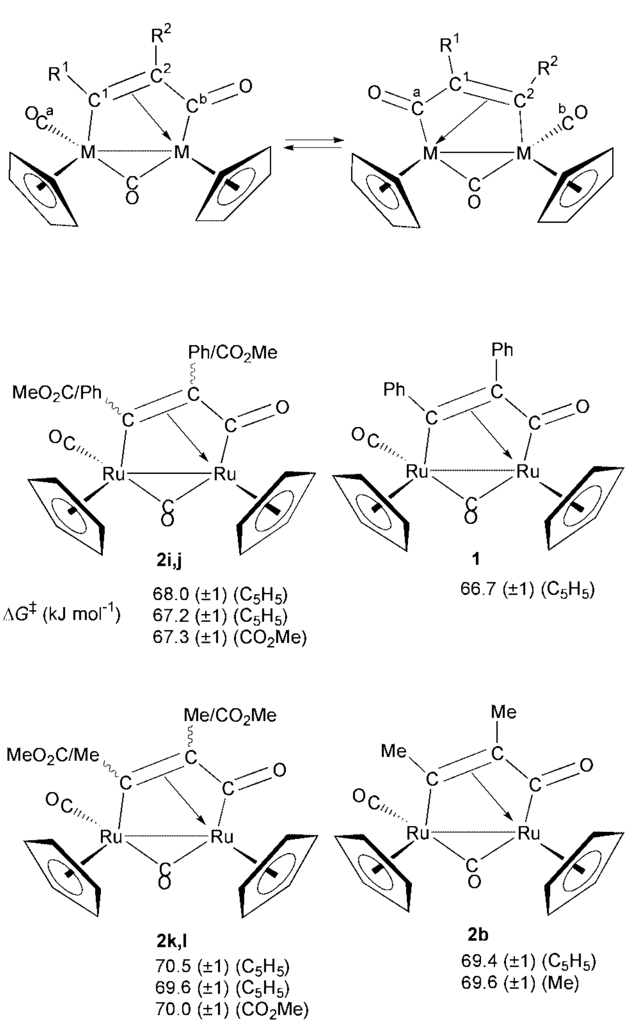


Fig. 1 $\Delta G^{\ddagger}$ values calculated for the ligands shown in parentheses.

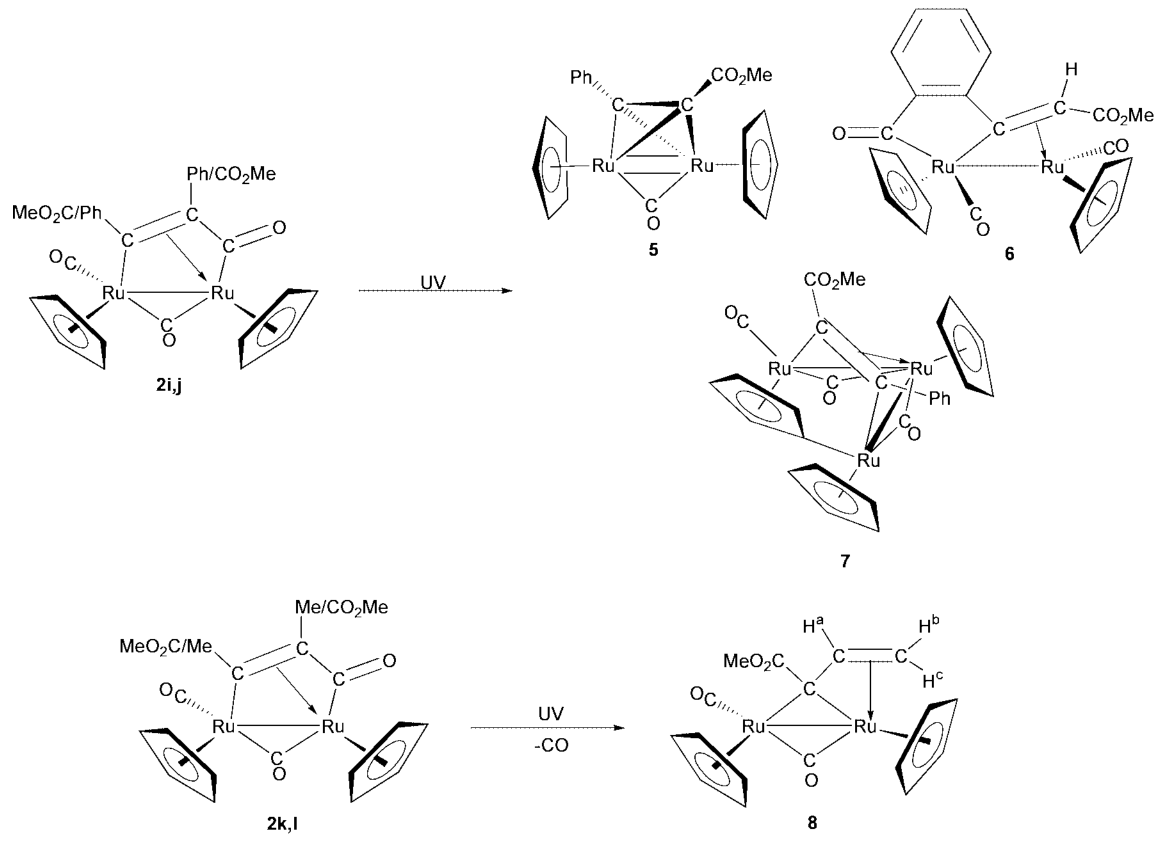
Free energies of activation for the process in **2i,j** and **2k,l** were calculated from the variable temperature NMR data and are given in Fig. 1 along with those established[1] for the symmetrical analogues **1** and **2b**. It can be seen that the $\Delta G^{\ddagger}$ values for **2i,j** and **2k,l** are effectively the same as those for **1** and **2b**, *i.e.* replacing a phenyl or a methyl group by the electron withdrawing methyl carboxylate group has little effect. This is in keeping with the proposal that electronic factors are less important than steric in determining the activation energy of the fluxional process.[1]

The *cis* and *trans* isomers of the μ-vinylidene complex $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C{=}C(H)CO_2Me\}(\eta\text{-}C_5H_5)_2]$ (**4c**) interconvert slowly at room temperature in dichloromethane, and solutions of the pure *cis* and *trans* isomers transform to an equilibrium mixture (*cis*:*trans* 5:2) over a period of two days. A similar situation has been observed for the parent ethenylidene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)(\eta\text{-}C_5H_5)_2]$ (**4a**), which exists in $[^2H_8]$-toluene at room temperature as an equilibrium mixture of *cis* and *trans* isomers in 6:5 ratio.[2] However, interconversion of the *cis* and *trans* isomers of the phenylvinylidene species $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C{=}C(H)Ph\}(\eta\text{-}C_5H_5)_2]$ (**4b**) faces a higher energy barrier, only occurring on warming to 70 °C to give an approximately 1:1 ratio at equilibrium.[2] This isomerisation process has been proposed to involve bridge opening and rotation about the metal–metal bond, similar to that originally reported for $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$[4] and subsequently proposed to occur for doubly bridged complexes in general.[5]

Photolysis reactions

Although the complexes **2i,j** and **2k,l** are thermally stable they display interesting reactivity when subjected to UV irradiation (see Scheme 3).

Photolysis of a toluene solution of **2i,j** for 20 h, followed by chromatography, led to isolation of green $[Ru_2(\mu\text{-}CO)\{\mu\text{-}\eta^2{:}\eta^2\text{-}C(Ph)C(CO_2Me)\}(\eta\text{-}C_5H_5)_2]$ (**5**) in 21% yield, orange $[Ru_2(CO)_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}C(O)C_6H_4C{=}C(H)CO_2Me\}(\eta\text{-}C_5H_5)_2]$ (**6**) in



Scheme 3 Photolysis of dimetallacyclopentenone complexes.

Table 3 Selected bond lengths (Å) and angles (°) for **6**

Ru(1)–C(3)	2.065(2)	C(4)–C(5)	1.394(3)
Ru(1)–C(10)	2.077(2)	C(5)–C(6)	1.383(4)
Ru(1)–Ru(2)	2.8238(9)	C(6)–C(7)	1.380(4)
Ru(2)–C(10)	2.118(2)	C(7)–C(8)	1.384(4)
Ru(2)–C(11)	2.190(2)	C(8)–C(9)	1.403(3)
O(3)–C(3)	1.212(3)	C(9)–C(10)	1.496(3)
C(3)–C(4)	1.493(3)	C(10)–C(11)	1.435(3)
C(4)–C(9)	1.390(3)	C(11)–C(12)	1.477(3)
C(3)–Ru(1)–C(10)	80.03(9)	C(4)–C(9)–C(10)	115.2(2)
C(3)–Ru(1)–Ru(2)	107.27(7)	C(11)–C(10)–C(9)	116.96(19)
C(10)–Ru(1)–Ru(2)	48.32(6)	C(11)–C(10)–Ru(1)	128.75(16)
C(10)–Ru(2)–C(11)	38.88(8)	C(9)–C(10)–Ru(1)	114.27(15)
C(10)–Ru(2)–Ru(1)	47.07(6)	C(11)–C(10)–Ru(2)	73.26(13)
C(11)–Ru(2)–Ru(1)	77.56(6)	C(9)–C(10)–Ru(2)	117.49(15)
C(12)–O(5)–C(13)	116.5(2)	Ru(1)–C(10)–Ru(2)	84.61(8)
O(3)–C(3)–C(4)	121.0(2)	C(10)–C(11)–C(12)	130.2(2)
O(3)–C(3)–Ru(1)	124.4(2)	C(10)–C(11)–Ru(2)	67.86(12)
C(4)–C(3)–Ru(1)	114.57(16)	C(12)–C(11)–Ru(2)	116.48(17)
C(9)–C(4)–C(3)	115.2(2)		

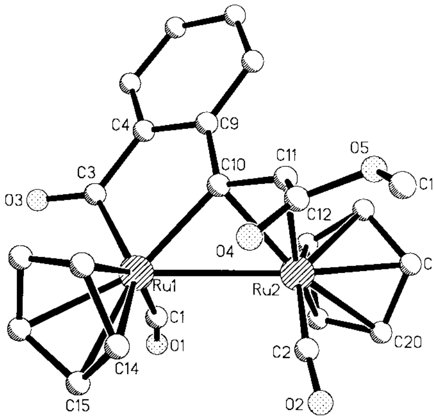


Fig. 2 Molecular structure of **6**, showing labelling scheme.

37% yield, and red [$Ru_3(CO)(\mu$-$CO)_2\{\mu^3$-η^2-C(Ph)C(CO_2Me)}-(μ-η^1:η^5-C_5H_4)(η-C_5H_5)$_2$] (**7**) in 8% yield.

The formation of the Ru=Ru double bonded μ-alkyne complex **5** was not unexpected, since complex **1** undergoes similar photochemically induced decarbonylation to afford the analogous [$Ru_2(\mu$-CO)$\{\mu$-η^2:η^2-C(Ph)C(Ph)}(η-C_5H_5)$_2$].[1,6] This allowed ready characterisation of **5** by comparison of spectroscopic data (*e.g.* bridging carbonyl band at 1759 cm^{-1} in the IR and single cyclopentadienyl resonance in the ^{1}NMR spectrum). However, X-ray diffraction studies were required to establish the structures of **6** and **7**, as described below.

Molecular structure of [$Ru_2(CO)_2\{\mu$-η^2:η^2-C(O)C_6H_4C=C(H)-$CO_2Me\}(\eta$-$C_5H_5)_2$] (6)

The molecular structure of **6** is illustrated in Fig. 2 and bond lengths and angles are presented in Table 3. Fig. 2 shows a *trans* arrangement of the cyclopentadienyl rings about the metal–metal bond with each ruthenium atom also carrying a terminal carbonyl ligand. The major interest in **6** attaches to the unique bridging ligand derived from cleavage of the alkyne–CO bond in **2i,j**, transfer of a proton from the *ortho* position of the phenyl ring to the C(11) of the alkyne, and formation of a carbon–carbon bond between the phenyl and a carbonyl group. Carbons C(3), C(4), C(9) and C(10) make up, along with Ru(1), a metallacyclopentenone ring which is attached to a phenyl ring made up of carbons C(4)–C(9) and having an exocyclic double bond [C(10), C(11)] η^2-co-ordinated to Ru(2). The two rings and the double bond of the bridging unit are approximately coplanar, with none of the constituent atoms deviating more than 0.0452 Å from the mean plane. The ligand can alternatively be viewed as an exotic form of a μ-vinyl ligand with the substituents on C(11) of the vinylic unit held in a *trans* orientation with the proton pointing away from the metal–metal bond. Complexes related to **6** have been synthesised before both in this laboratory (*e.g.* [$Ru_2(CO)_2\{\mu$-η^2:η^2-C(Me)C(H)C(H)$_2$C=CH$_2$}-(η-C_5Me_5)$_2$][7]) and by other groups (*e.g.* [$Fe_2(CO)_2\{\mu$-η^2:η^2-C(O)C(Ph)C(Ph)C=CH$_2$}(η-C_5H_5)$_2$][8]).

Table 4 Selected bond lengths (Å) and angles (°) for **7**

Ru(1)–C(4)	2.090(5)	C(4)–C(5)	1.488(7)
Ru(1)–Ru(2)	2.7754(11)	C(11)–C(12)	1.505(7)
Ru(2)–C(4)	2.158(5)	C(14)–C(18)	1.443(8)
Ru(2)–C(11)	2.162(5)	C(14)–C(15)	1.445(8)
Ru(2)–Ru(3)	2.8076(10)	C(15)–C(16)	1.417(8)
Ru(3)–C(11)	2.067(5)	C(16)–C(17)	1.423(9)
Ru(3)–C(14)	2.072(6)	C(17)–C(18)	1.413(9)
C(4)–C(11)	1.416(7)		
C(4)–Ru(1)–C(14)	86.7(2)	C(5)–C(4)–Ru(1)	121.2(3)
C(4)–Ru(1)–Ru(2)	50.27(14)	C(11)–C(4)–Ru(2)	71.0(3)
C(14)–Ru(1)–Ru(2)	84.68(14)	C(5)–C(4)–Ru(2)	130.8(4)
C(4)–Ru(2)–C(11)	38.28(19)	Ru(1)–C(4)–Ru(2)	81.57(17)
C(4)–Ru(2)–Ru(1)	48.16(13)	C(4)–C(11)–C(12)	117.7(4)
C(11)–Ru(2)–Ru(1)	72.72(14)	C(4)–C(11)–Ru(3)	126.1(4)
C(4)–Ru(2)–Ru(3)	76.58(13)	C(12)–C(11)–Ru(3)	115.9(4)
C(11)–Ru(2)–Ru(3)	46.96(14)	C(4)–C(11)–Ru(2)	70.7(3)
Ru(1)–Ru(2)–Ru(3)	77.79(2)	C(12)–C(11)–Ru(2)	124.9(4)
C(11)–Ru(3)–C(14)	84.3(2)	Ru(3)–C(11)–Ru(2)	83.18(18)
C(11)–Ru(3)–Ru(2)	49.86(14)	C(18)–C(14)–C(15)	104.0(5)
C(14)–Ru(3)–Ru(2)	86.52(14)	C(18)–C(14)–Ru(3)	127.8(4)
C(11)–C(4)–C(5)	121.9(4)	C(15)–C(14)–Ru(3)	126.5(4)
C(11)–C(4)–Ru(1)	114.3(4)	Ru(3)–C(14)–Ru(1)	109.7(2)

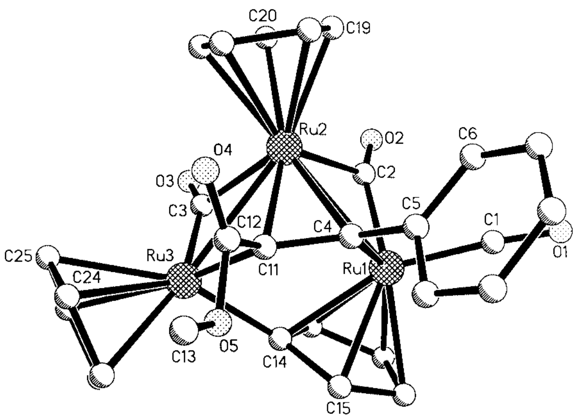


Fig. 3 Molecular structure of **7**, showing labelling scheme.

Molecular structure of [$Ru_3(CO)(\mu$-$CO)_2\{\mu_3$-η^2-C(Ph)C-(CO_2Me)}(μ-η^1:η^5-C_5H_4)(η-C_5H_5)$_2$] (7)

The molecular structure of **7** is illustrated in Fig. 3 and bond lengths and angles are presented in Table 4.

The three metal atoms form a V-shaped arrangement with the two non-bonded rutheniums Ru(1) and Ru(3) being separated by a distance of 3.506(4) Å, correlating well with a non-bonding M–M distance of 3.659 Å found for the triruthenium species [$P(Ph_3)_2$][$Ru_3(CO)_9(\mu$-Cl)(μ_3-η^2-PhC_2Ph)].[9] The metal core is bridged by the methyl phenylpropiolate unit, with the C(4)–C(11) backbone parallel to the non-bonding Ru(1)–Ru(3) vector, acting as a π-donor to Ru(2) and a σ-donor to both Ru(1) and Ru(3). This μ_3-(η^2-||) mode of co-ordination is as expected for a trimetallic complex having 50 electrons.[10]

Formally, Ru(2) is a 19 electron centre and Ru(3) a 17 electron centre, but the two bridging carbonyl ligands show a degree of semi-bridging character which implies that each metal atom achieves an 18 electron configuration. Thus, the Ru(1)–C(2) bond length is 1.962(6) Å compared with the Ru(2)–C(2) length of 2.279(6) Å and the bond between Ru(2) and C(3) [2.285(6) Å] is long compared to that between Ru(3) and C(3) [1.905(6) Å]. The Ru(1)–C(2)–O(2) and Ru(3)–C(3)–

O(3) angles of 150.0(5) and 151.6(5)°, respectively, support this view. The two non-bonded ruthenium atoms are bridged by a cyclopentadienylidene unit which is σ-bound to Ru(3) and η^5-bound to Ru(1). This ring shows a slight departure, in its C–C bond distances and internal angles, from the five-fold symmetry displayed by cyclopentadienyl ligands bound to metal atoms in a terminal fashion. Thus, the ring has become slightly elongated resulting in a lengthening of the C(14)–C(18) and C(14)–C(15) bonds and a closing of the C(18)–C(14)–C(15) bond angle. This pattern is consistent with that seen for μ-C_5H_4 groups in several other complexes.[11] The asymmetric nature of the alkyne unit in complex **7** gives rise to the possibility of isomers in which the phenyl and carboxylate substituents have effectively swapped places. However, only the isomer shown in Fig. 3 is observed in both the solid state and in solution. The reason for this selectivity is not clear but may be due to steric effects. Exchanging the two R groups would place the larger of the two (the phenyl group) between the cyclopentadienyl rings attached to Ru(2) and Ru(3) in a *cis* arrangement. This would be energetically less favourable than having the phenyl ring at the other alkyne site where the cyclopentadienyl rings on Ru(1) and Ru(2) are constrained in a *trans* arrangement by the metallation of the cyclopentadienyl unit attached to Ru(1).

The solid state structures of **6** and **7** are maintained in solution. Thus, the IR spectrum of complex **6** shows carbonyl stretches at 1967 and 1936 (terminal), 1718 (acyl) and 1626 (carboxylate) cm^{-1} while **7** displays bands at 1971 (terminal), 1839, 1799 (bridging) and 1697 (carboxylate) cm^{-1}. The ^1H NMR spectrum of **6** shows resonances for the proton on the bridging vinyl group at δ 5.95 (s, 1H), for inequivalent cyclopentadienyl groups, and for the protons of the C_6H_4 ring. In the ^1H NMR spectrum of **7** the protons of the bridging cyclopentadienylidene unit appear at δ 5.36 (m, 1H), 5.35 (m, 1H), 5.23 (m, 1H) and 4.66 (m, 1H) agreeing well with those for the dizirconium complex $[Zr_2(PPh_2Me)_2(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)_2(\eta\text{-}C_5H_5)_2]$,[12] while the two inequivalent cyclopentadienyl groups are seen at δ 5.00 (s, 5H) and 4.94 (s, 5H). In the ^{13}C-{^1H} spectrum the μ-C carbon of the bridging cyclopentadienylidene showed a signal at δ 118.5 while the other carbons in the ring were assigned based on suggestions by Davison and Wreford.[13]

Complex **6** is an isomer of **2i**,**j** and a plausible pathway for its formation has it arising from **2j** in four steps: (a) the phenyl ring undergoes orthometallation (*i.e.* oxidative addition) at a temporarily unsaturated ruthenium centre, followed by (b) linking of the *ortho* carbon with a terminal carbonyl ligand, (c) transfer of the ruthenium hydride ligand to the $C(CO_2Me)$ carbon, and (d) cleavage of the alkyne–CO bond. The order in which (b)–(d) occurs is not clear. In contrast, the formation of complex **5** from **2i**,**j** clearly arises by a straightforward decarbonylation process, inducing C–C bond cleavage. It might be envisaged that the trinuclear complex **7** is formed *via* addition of a free radical fragment such as $[Ru(CO)_2(\eta\text{-}C_5H_5)]$ across the unsaturated metal–metal bond of the diruthenium complex **5**, since a similar process involving addition of monometallic fragments across a ruthenium–ruthenium double bond has been effected in this laboratory, leading to the formation of a range of trinuclear μ_3-alkyne complexes.[14] If this suggestion were correct, initial formation of **5** from **2i**,**j** might be expected, with a build up of **7** at longer time. However, varying the time of photolysis affects only the yields of the products **5**–**7**, which reach a maximum after 20 h, and does not significantly change their ratios, strongly suggesting that they are formed from **2i**,**j** *via* distinct pathways.

As expected, the yield of complex **5**, formed by decarbonylation, was increased by subjecting a tetrahydrofuran solution of **2i**,**j** to UV irradiation for 20 h while purging slowly with nitrogen to sweep away liberated CO; **5**, **6** and **7** were isolated in yields of 33, 21 and 3%, respectively.

When a toluene solution of a mixture of isomers **2k**,**l** was irradiated with UV light the orange complex $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(CO_2Me)CH{=}CH_2\}(\eta\text{-}C_5H_5)_2]$ (**8**) was obtained in 35% yield as the only product, as shown in Scheme 3. Vinylalkylidene complexes like **8** have been synthesised in this laboratory by a variety of routes,[15] and characterisation of **8** from its spectroscopic data was therefore straightforward. In particular, in the ^1H NMR spectrum a characteristic high field signal at δ −0.11 is observed for H^c, reflecting its position close to the Ru–Ru bond. The formation of complex **8** involves loss of a CO, cleavage of the alkyne–CO bond and a proton migration from the methyl group to the adjacent carbon, allowing coordination of the vinyl group, but the order in which these steps occur is again uncertain.

Only complexes of type **5** have previously been obtained from UV irradiation of dimetallacyclopentenones $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2R_2\}(\eta\text{-}C_5H_5)_2]$ (**2a**–**h**) and the presence of a methylcarboxylate group is therefore seen to have a significant influence on the photolytic reactivity of these complexes. The subtlety of the effect is highlighted by the fact that: (i) only complexes **2i**,**j** give the metallacyclic species **6** upon irradiation whereas any dimetallacyclopentenone species **2** containing a phenyl group could in principle give this type of compound; (ii) only complexes **2k**,**l** give the vinylalkylidene complex **8** whereas any dimetallacyclopentenone of type **2** containing a methyl group could give such a species; and (iii) only the PhC_2CO_2Me-derived dimetallacycles **2i**,**j** afford the triruthenium complex **7** whereas no such complex is observed from photolysis of the MeC_2CO_2Me-derived **2k**,**l**.

Experimental

Reactions and general manipulations were performed under a nitrogen atmosphere using deoxygenated solvents, dried by distillation over an appropriate drying agent. Photolysis reactions were carried out in silica glass tubes held *ca.* 20 cm away from a 500 W mercury vapour lamp as a source of UV irradiation. Column chromatography was performed on alumina (Brockmann activity II). Reactions were routinely monitored by IR spectroscopy. Solution IR spectra were recorded on a Perkin-Elmer 1710 Fourier Transform Spectrometer using calcium fluoride cells of 1 mm path length. Low resolution electron impact mass spectra and FAB mass spectra were recorded using a Fisons Autospec instrument. Proton and carbon-13 NMR spectra were recorded on JEOL GX 270 and GX 400 spectrometers. All NMR spectrometers operated in the Fourier Transform mode, with field stability maintained by an external lock system. Elemental analyses were performed by the Microanalytical Laboratory of the School of Chemistry, University of Bristol.

The free energies of activation for the processes in **2i**,**j** and **2k**,**l** were calculated from the variable temperature NMR data, recorded in [$^2H_5$]-pyridine, using the expression $\Delta G^{\ddagger} = -RT_c\ln(2\pi\Delta\nu h/kT_c[3\{1+\sqrt{3}(p_a - p_b)\}]^{0.5})$, where T_c = coalescence temperature, $\Delta\nu$ = chemical shift separation of the exchanging nuclei and p_a, p_b = fractional population of the two sites.[16]

Methyl phenylpropiolate (Lancaster), methyl 2-butynoate (Fluka) and methyl propiolate (Aldrich) were used as supplied. The complex $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}(\eta\text{-}C_5H_5)_2]$ (**1**) was prepared by the literature method.[1]

Reaction of $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}(\eta\text{-}C_5H_5)_2]$ (1) with PhC_2CO_2Me

A toluene solution (150 cm^3) of **1** (1.00 g, 1.67 mmol) and methyl phenylpropiolate (2.0 cm^3, 14.37 mmol) was heated at reflux for 10 min. Removal of solvent and chromatography of the crude product, eluting with dichloromethane–hexane (1 : 1), gave an orange band. Removal of solvent under reduced pressure yielded an orange microcrystalline mixture of [Ru$_2$(CO)(μ-CO){μ-C(O)C$_2$(CO$_2$Me)Ph}(η-C$_5$H$_5$)$_2$] (**2i**,**j**) (757 mg, 73%), which was further purified by recrystallisation from a hexane-layered dichloromethane solution.

Reaction of [Ru$_2$(CO)(μ-CO){μ-C(O)C$_2$Ph$_2$}(η-C$_5$H$_5$)$_2$] (1) with MeC$_2$CO$_2$Me

A toluene solution (150 cm^3) of **1** (1.00 g, 1.67 mmol) and methyl 2-butynoate (1.0 cm^3, 10 mmol) was heated at reflux for 10 min. Removal of solvent and chromatography of the resulting residue, eluting with dichloromethane–hexane (3 : 2), developed an orange band which gave 515 mg (60%) of [Ru$_2$(CO)(μ-CO){μ-C(O)C$_2$(CO$_2$Me)Me}(η-C$_5$H$_5$)$_2$] (**2k**,**l**) as an orange-red solid.

Reaction of [Ru$_2$(CO)(μ-CO){μ-C(O)C$_2$Ph$_2$}(η-C$_5$H$_5$)$_2$] (1) with HC$_2$CO$_2$Me

A toluene solution (150 cm^3) of **1** (1.00 g, 1.67 mmol) and methyl propiolate (2.0 cm^3, 16.50 mmol) was heated to reflux for 4 h, during which time a colour change from orange to brown occurred. Removal of the solvent and chromatography of the crude product separated three bands. The first band (yellow) eluted with hexane and was identified as *trans*-[Ru$_2$(CO)$_2$(μ-CO){μ-C=C(H)CO$_2$Me}(η-C$_5$H$_5$)$_2$] *trans*-**4c** (53 mg, 8%). The second band (orange) eluted with dichloromethane–hexane (1 : 9) and gave *ca.* 5 mg of an unidentified orange complex which rapidly decomposed, both as a solid and in solution, to yield a black oil. The third band (yellow) eluted with dichloromethane–hexane (1 : 1) and afforded *cis*-[Ru$_2$(CO)$_2$(μ-CO){μ-C=C(H)CO$_2$Me}(η-C$_5$H$_5$)$_2$] *cis*-**4c** (332 mg, 48%) as a yellow solid.

Isomerisation of *trans*-[Ru$_2$(CO)$_2$(μ-CO){μ-C=C(H)CO$_2$Me}(η-C$_5$H$_5$)$_2$] *trans*-4c. A dichloromethane solution of *trans*-**4c** was left to stand at room temperature. After 48 h the solvent was removed and a ^{1}H NMR spectrum of the yellow residue recorded, showing a mixture of *cis*- and *trans*-**4c** in the ratio *ca.* 5 : 2.

Isomerisation of *cis*-[Ru$_2$(CO)$_2$(μ-CO){μ-C=C(H)CO$_2$Me}(η-C$_5$H$_5$)$_2$] *cis*-4c. A dichloromethane solution of *cis*-**4c** was left to stand at room temperature. Removal of the solvent, after 48 h, gave a yellow solid which was identified by ^{1}H NMR spectroscopy as a mixture of *cis*- and *trans*-**4c** in *ca.* 5 : 2 ratio.

Photolysis of [Ru$_2$(CO)(μ-CO){μ-C(O)C$_2$(CO$_2$Me)Ph}(η-C$_5$H$_5$)$_2$] (2i,j)

UV irradiation of a toluene solution (150 cm^3) of **2i**,**j** (740 mg, 1.28 mmol) for 20 h resulted in a darkening of the colour from red-orange to red-brown. Removal of solvent and chromatography of the residue separated the following bands: (i) pale pink, eluted with dichloromethane–hexane (1 : 9), provided a red solid (50 mg, 8%) identified as [Ru$_3$(CO)(μ-CO)$_2${μ^3-η^2-C(Ph)C(CO$_2$Me)}(μ-σ : η^5-C$_5$H$_4$)(η-C$_5$H$_5$)$_2$] (**7**); (ii) green, eluted with dichloromethane–hexane (1 : 1), gave [Ru$_2$(μ-CO){μ-C$_2$(CO$_2$Me)Ph}(η-C$_5$H$_5$)$_2$] (**5**) (138 mg, 21%) as a dark green powder; (iii) orange, eluted with dichloromethane–hexane (1 : 1), gave orange crystalline [Ru$_2$(CO){μ-C(O)C$_6$H$_4$C=CH(CO$_2$Me)}(η-C$_5$H$_5$)$_2$] (**6**) (272 mg, 37%).

Photolysis of [Ru$_2$(CO)(μ-CO){μ-C(O)C$_2$(CO$_2$Me)Ph}(η-C$_5$H$_5$)$_2$] (2i,j) while purging with nitrogen

A tetrahydrofuran solution (150 cm^3) of **2i**,**j** (740 mg, 1.28 mmol) was irradiated with UV light for 20 h while purging with a slow stream of nitrogen. Removal of the solvent and chromatography of the red-brown residue led to the isolation of the following products: (i) red [Ru$_3$(CO)(μ-CO)$_2${μ$_3$-η^2-C(Ph)C(CO$_2$Me)}(μ-σ:η^5-C$_5$H$_4$)(η-C$_5$H$_5$)$_2$] (**7**) (20 mg, 3%), eluted with dichloromethane–hexane (1 : 9); (ii) green [Ru$_2$(μ-CO){μ-C$_2$(CO$_2$Me)Ph}(η-C$_5$H$_5$)$_2$] (**5**) (218 mg, 33%), eluted with dichloromethane–hexane (1 : 1); (iii) orange [Ru$_2$(CO){μ-C(O)C$_6$H$_4$C=CH(CO$_2$Me)}(η-C$_5$H$_5$)$_2$] (**6**) (158 mg, 21%), eluted with dichloromethane–hexane (1 : 1).

Table 5 Crystallographic data for complexes **6** and **7**

	7·CH$_2$Cl$_2$	**6**
Formula	C$_{29}$H$_{24}$Cl$_2$O$_5$Ru$_3$	C$_{23}$H$_{18}$O$_5$Ru$_2$
M	826.6	576.5
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
a/Å	9.258(2)	14.461(5)
b/Å	10.657(2)	9.755(4)
c/Å	15.409(3)	15.217(5)
a/°	71.22(3)	90
β/°	81.21(3)	109.74(3)
γ/°	82.32(3)	90
U/Å^3	1416.6(5)	2020.5(13)
Z	2	4
Reflections measured	5321	5029
Unique reflections	4984	4852
R_{int}	3.0%	1.9%
μ/mm^{-1}	1.81	1.53
wR_2 (all data)	0.097	0.061
Number of observed [$F^2 > 2\sigma(F^2)$] data	4299	4468
R_1 (observed data)	0.037	0.024

Photolysis of [Ru$_2$(CO)(μ-CO){μ-C(O)C$_2$(CO$_2$Me)Me}(η-C$_5$H$_5$)$_2$] (2k,l)

Irradiation of a toluene solution (100 cm^3) of **2k**,**l** (300 mg, 0.58 mmol) resulted in a gradual colour change from orange to red. Removal of the solvent and chromatography of the crude product separated four bands. The first two bands, both yellow, eluted with hexane and yielded two oily products which were not characterised. The third, orange band eluted with dichloromethane–hexane (1 : 1) and afforded 100 mg (35%) of crystalline [Ru$_2$(CO)(μ-CO){μ-C(CO$_2$Me)C(H)=CH$_2$}(η-C$_5$H$_5$)$_2$] (**8**). A fourth, brown band eluted with acetone and yielded a brown oil which was not characterised.

X-Ray analyses of complexes 6 and 7

Many of the details of the structure analyses carried out on complexes **6** and **7** are listed in Table 5. In each case a single crystal was mounted in vacuum grease on a glass fibre. Crystallographic data were collected at room temperature on a Siemens R3/mV diffractometer using graphite monochromated Mo-K$_\alpha$ radiation (λ = 0.7107 Å). No crystal decay was observed over the data collection period. Empirical absorption corrections were applied based on azimuthal scan data. The structures were solved variously by heavy atom and direct methods and refined by least squares on F^2 values for all reflections with weighting $w^{-1} = \sigma^2(F_o^2)+(aP)^2+bP$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.[17] The largest features in the electron density difference map for **7** are close to the dichloromethane solvent indicating that this molecule is disordered. Attempts to refine this disorder were made using a number of models but none gave satisfactory results.

CCDC reference number 186/2079.

See http://www.rsc.org/suppdata/dt/b0/b003156i/ for crystallographic files in .cif format.

Acknowledgements

We thank the EPSRC for the award of Research Studentships to P. J. K. and G. J. M.

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