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FULL PAPER

Oligomerisation of alkynes at a pentamethylcyclopentadienylruthenium centre †

Michael I. Bruce,*[a] Ben C. Hall,[a] Brian W. Skelton,[b] Allan H. White[b] and Natasha N. Zaitseva[a]

[a] *Department of Chemistry, University of Adelaide, Adelaide, South Australia 5005, Australia. E-mail: michael.bruce@adelaide.edu.au*
[b] *Department of Chemistry, University of Western Australia, Nedlands, Western Australia 6907, Australia*

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Reactions between the neutral vinylidene RuCl(=C=CHPh)(PPh_3)Cp* **2** and AgC≡CCO_2Me gave Ru{η^1-C(C≡CPh)=CHC(O)OMe-*O*}(PPh_3)Cp* **3**, while either LiC≡CPh or HC≡CPh/NaOMe afforded the known Ru{η^3-PhCHCHC=CPh(C≡CPh)}(PPh_3)Cp* **1**. Similarly, RuCl{=C=CH(CO_2Me)}(PPh_3)Cp* **4** reacted with HC≡CPh/NaOMe to give Ru{η^3-CH(CO_2Me)CHC=CPh(C≡CCO_2Me)}(PPh_3)Cp* **5**. Complex **3** reacted with HC≡CCO_2R (R = Me or Et) to give the 1,3,4,5-tetraen-1-yls Ru{η^1,η^2-C(CO_2R)=CHCPh=C=C=CH(CO_2Me)}(PPh_3)Cp* (R = Me **6** or Et **7**)] and with HC≡$CSiMe_3$ to give a mixture of Ru{η^3-CH(CO_2Me)C(CH=CHSiMe_3)C=CPhC≡C$SiMe_3$}(PPh_3)Cp* **8** and Ru{η^3-CH(CO_2Me)CHC=CPh(C≡C$SiMe_3$)}(PPh_3)Cp* **9**. Crystal structures of **1**, **3** and **5**–**8** were determined. These reactions provide routes to the stepwise formation of novel non-cyclic oligomers of 1-alkynes, with **8** containing the first example derived from four alkynes.

Introduction

We have recently described the preparation of some neutral vinylideneruthenium complexes containing the RuCl(PPh_3)Cp* moiety from RuCl(PPh_3)$_2$Cp* and the alkyne in non-polar solvents.[1] In contrast to the reactions between RuCl(PPh_3)$_2$Cp and 1-alkynes, which are usually carried out in methanol, thus allowing dissociation of chloride and formation of the cationic vinylidene complexes,[2] the present route depends on dissociation of one of the bulky PPh_3 ligands in place of chloride and gives access to compounds of the type RuCl(=C=CHR)(PPh_3)Cp*. Subsequent reactions in the presence of base (NaOMe or $NHMe_2$) and another ligand, L (≠ PPh_3), have afforded chiral complexes Ru(C≡CR)(L)(PPh_3)Cp* by formal 1,3 elimination of HCl.[3] These complexes were formed with a variety of ligands, including CO, C_2H_4, O_2 and S_2. Addition of cationic electrophiles to the alkynyl compounds gives the corresponding cationic vinylidene complexes.

The finding that $RuH_3(PR_3)Cp^*$ (R = Ph, Cy or Me) are effective catalysts for the dimerisation of 1-alkynes to 1,3- and *cis*- and *trans*-1,4-enynes has been interpreted in terms of coupling of alkynyl and vinylidene ligands at the ruthenium centre, the stereochemistry being determined by the orientation of the vinylidene.[4] It was noted also that 1,2,3-trienes were obtained from HC≡CR (exclusively for R = CH_2Ph, 16% for R = Bu^t) and that trimers or higher oligomers were obtained with smaller alkynes. Later, it was found that the 16-electron complex Ru(C≡CPh)(PPh_3)Cp* catalysed the dimerisation of HC≡CR (R = Ph or CO_2Me); the novel allylic complex, Ru{η^3-PhCHCHC=CPh(C≡CPh)}(PPh_3)Cp* (**1**; Scheme 1), with a trimer of the alkyne, was obtained as a metal-containing product.[5,6] The 16-electron complex may be solvated or possess an agostic Ru···H interaction, as found spectroscopically for the product obtained from RuCl(=C=CHBu^t)(PPh_3)Cp* and C_2Me_2.[7]

Independently, we have found that complex **1** is formed in the reaction between RuCl(=C=CHPh)(PPh_3)Cp* **2** and an excess of HC≡CPh in the presence of NaOMe. Further examination of this general reaction and the use of alkynyl anions as reagents has resulted in the formation of complexes containing organic ligands derived from two, three or four molecules of alkyne, formed in stepwise reactions and therefore able to be used in the formation of derivatives containing several different alkynes. The organic ligands are linear or branched oligomers and these reactions represent a novel method of coupling alkynes at a ruthenium centre.

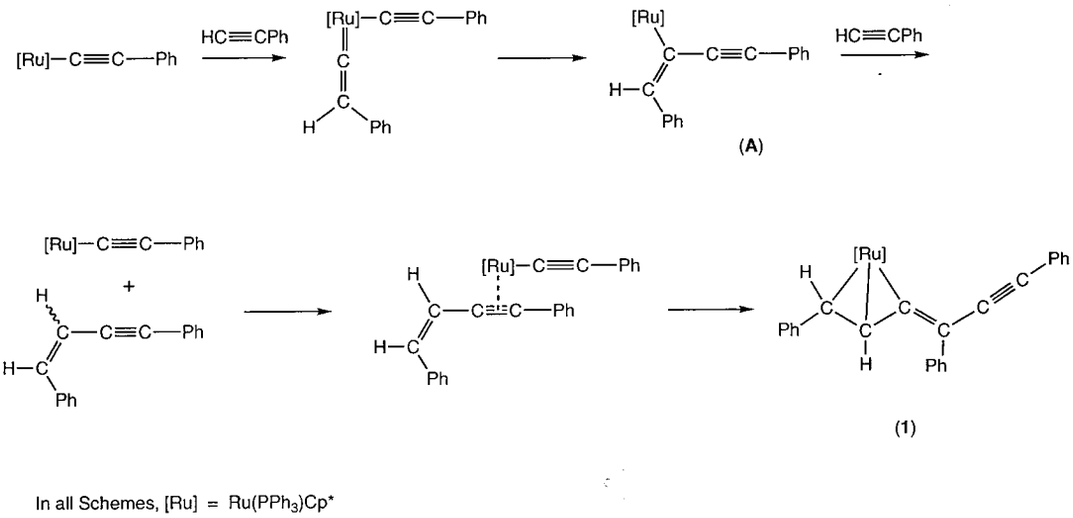
These studies provide further examples of combination of alkynes at a Group 8 metal centre to give non-cyclic products. While there have been many studies of the coupling of alkynyl and vinylidene ligands to give butenynyl complexes or, more rarely, the isomeric butatrienyl derivatives,[8,9] incorporation of more than two alkynes in the products has received much less attention. Some years ago ruthenium complexes containing both alkynyl and η^3-enynyl ligands were found to undergo coupling to give alkynylbutadienyl ligands in reactions which are related to those described below.[10] More recently, tri-[11] and tetramerisation[12] of alkynes on rhodium complexes have been reported.

Results

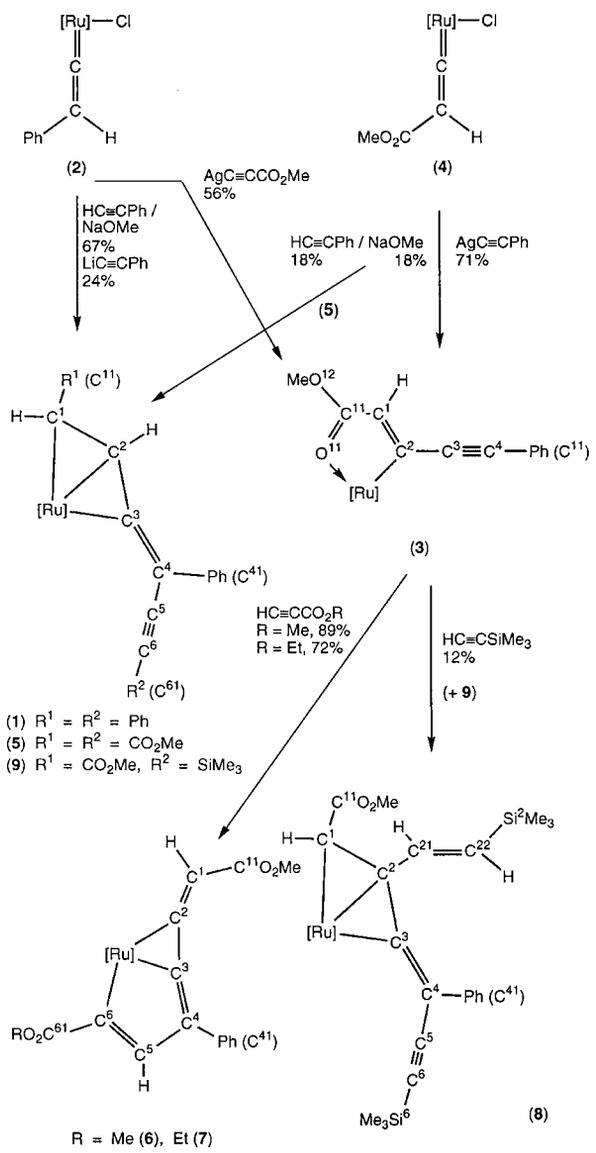
The reactions to be described below are summarised in Scheme 2. Instead of the expected complex Ru(C≡CPh)(η-HC_2Ph)(PPh_3)Cp*, or possibly the analogous phenylvinylidene derivative, the reaction between RuCl(=C=CHPh)(PPh_3)Cp* **2** and phenylethyne, carried out in the presence of NaOMe, afforded a yellow solid. We have determined the structures of two crystalline forms, one of which was the 1.5-benzene solvate described independently by others,[5] whose composition corresponded to the incorporation of two additional HC≡CPh molecules into **2**, namely Ru{η^3-PhCHCHC=CPh(C≡CPh)}(PPh_3)Cp* **1**. The second form is solvent-free and both structures are experimentally identical. The same complex could be isolated, in lower yield, from a reaction between **2** and LiC≡CPh.

In order to find out more about these unusual systems, we next examined the reaction between complex **2** and AgC≡

† Dedicated to Professor Helmut Werner, a respected and admired friend and colleague, on the occasion of his birthday.



Scheme 1



Scheme 2

CCO_2Me. A red-brown complex was isolated in 56% yield and identified as Ru{η^1-C(C≡CPh)=CHC(O)OMe-*O*}(PPh_3)Cp* **3** by an X-ray structural determination. This material was also formed from the reaction between RuCl{=C=CH(CO_2Me)}(PPh_3)Cp* **4**[13] and AgC≡CPh. Treatment of **4** with NaOMe in the presence of an equimolar amount of HC≡CPh gave a mixture of **1** and **3**. The spectroscopic properties of **3** were consistent with its solid-state structure, with bands in the IR spectrum at 2163, 1724 and 1558 cm^{-1} being assigned to ν(C≡C), ν(CO) and ν(C=C) absorptions, respectively. In the ^{1}H NMR spectrum, doublet resonances at δ 1.40 and 6.25, having relative intensities 15/1, were assigned to the Cp* and =CH protons, respectively. The CO_2Me protons gave rise to a singlet resonance at δ 3.33 and the Ph multiplet was between δ 7.17 and 7.50. The ^{13}C NMR spectrum contained signals for Cp* (δ 10.82 and 86.99) and CO_2Me groups (δ 52.80 and 181.26), as well as for the two C≡C (δ 99.05 and 100.57) and =CH carbons (δ 122.97). The ion $[M - H]^+$ was present in the electrospray (ES) mass spectrum.

A different complex incorporating two additional alkyne molecules was formed from **1** and HC≡CCO_2Me in the presence of NaOMe. This was identified as Ru{η^3-CH(CO_2Me)CHC=CPh(C≡CCO_2Me)}(PPh_3)Cp* **5** by means of a single-crystal X-ray structural study, and was accompanied by a small amount of **3**. The IR spectrum of **5** contained bands assigned to ν(C≡C) at 2186, ν(CO) at 1706 and ν(C=C) at 1616 and 1594 cm^{-1}, while two singlets in the ^{1}H NMR spectrum at δ 3.70 and 3.94 indicated the presence of two non-equivalent CO_2Me groups. Other resonances included a doublet at δ 1.47 (Cp*) and two double doublets at δ 2.27 and 3.59 for the two CH protons. In the ^{13}C NMR spectrum the Cp* (δ 9.16 and 93.67), CO_2Me (δ 50.52, 52.32 and 217.0; the two ester CO resonances are accidentally equivalent) and C≡C carbons (δ 79.43 and 94.05) were accompanied by resonances at δ 112.11, 139.33, 155.55 and 174.73, assigned to the carbons of the C_4 chain. From solutions containing NaOMe, the highest ion in the ES mass spectrum was $[M + Na]^+$ at *m/z* 791.

Complex **3** reacts with HC≡CCO_2R (R = Me or Et) to give the 1,3,4,5-tetraenyl complexes Ru{η^1,η^2-C(CO_2R)=CHCPh=C=C=CH(CO_2Me)}(PPh_3)Cp* (R = Me **6** or Et **7**), each obtained as a single product. Both complexes were characterised by single-crystal structure determinations and their spectroscopic properties were consistent with these structures. The Cp* proton doublets are at δ 1.56 (R = Me) and 1.52 (Et), while the common CO_2Me groups are found at δ 3.33 and 3.37, respectively. This assignment is assisted by replacement of the CO_2Me signal at δ 3.29 in the ^{1}H NMR spectrum of **6** by the CH_2 multiplet at δ 3.61 for **7**.

Finally, a complex containing an organic ligand derived from four alkyne molecules is obtained when **3** is treated with HC≡$CSiMe_3$. The only tractable product was yellow crystalline Ru{η^3-CH(CO_2Me)C(CH=CHSiMe_3)C=CPhC≡C$SiMe_3$}(PPh_3)Cp* **8**, characterised by an X-ray structural study. This complex has spectroscopic properties consistent with its solid-

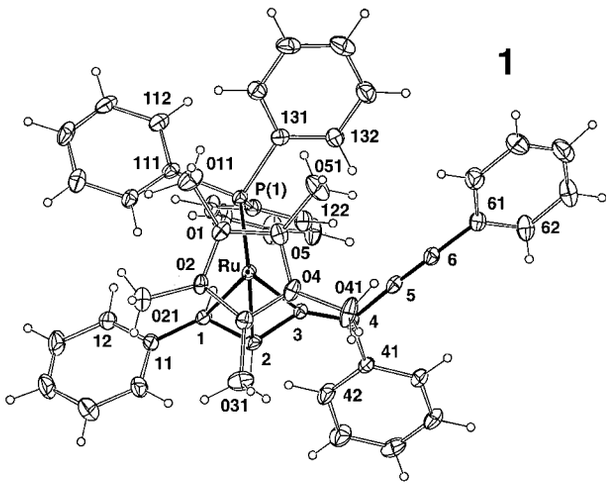


Fig. 1 Plot of molecule **1** of Ru{η^3-PhCHCHC=CPh(C≡CPh)}-(PPh_3)Cp* **1**, showing the atom numbering scheme.

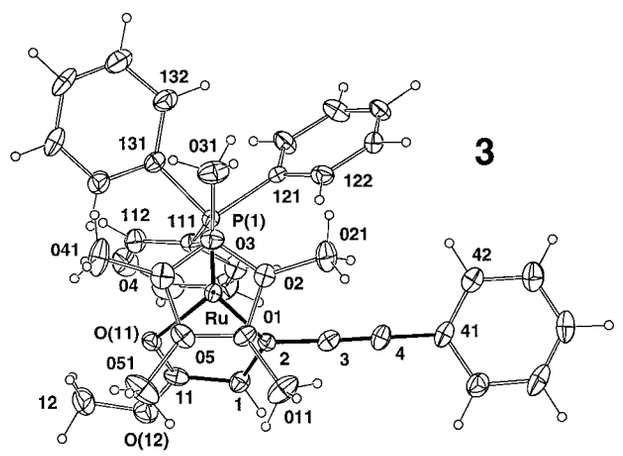
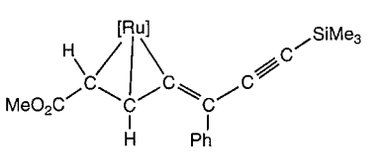


Fig. 2 Plot of a molecule of Ru{η^1-C(C≡CPh)=CHC(O)OMe-*O*}-(PPh_3)Cp* **3**, showing the atom numbering scheme.

state structure, with a single ν(C≡C) band at 2115 and a ν(CO) absorption at 1699 cm^{-1}. In the ^{1}H NMR spectrum, appropriate signals can be assigned to $SiMe_3$ (δ −0.23, 0.46), Cp* (1.47), CO_2Me (3.59) and CH protons (5.46, 6.66 and one beneath the Ph multiplet). The ES mass spectrum contains M^+ at *m*/*z* 880. The ES mass spectrum of a second product, which could only be obtained as a yellow oil which was unstable in solution, contained M^+ at *m*/*z* 782 and singlet resonances at δ −0.74, 1.66 and 3.53 which we assign to $SiMe_3$, Cp* and CO_2Me protons, respectively. These data are consistent with the formulation Ru{η^3-CH(CO_2Me)CHC=CPhC≡CSiMe_3}-(PPh_3)Cp* **9** and its formation can be accounted for by reactions analogous to those leading to complex **5** (see below).



(9)

Molecular structures of complexes 1, 3, 5, 6, 7 and 8

Plots of single molecules of each of these complexes are given in Figs. 1–5 and selected structural data are collected in Table 1. All contain an Ru(PPh_3)Cp* fragment supporting the various organic ligands. The geometrical parameters for this moiety are similar to those found in a variety of related structures which have been reported previously, with Ru–P between 2.311(2) and 2.338(1) Å and Ru–C(Cp*) between 2.203(5) and 2.368(7) Å,

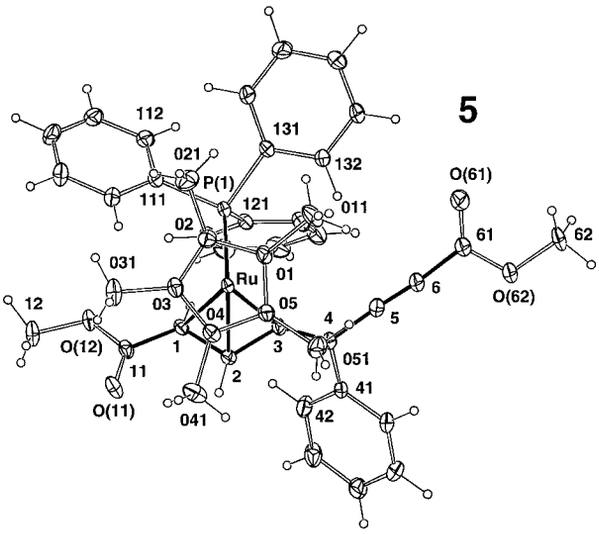


Fig. 3 Plot of a molecule of Ru{η^3-CH(CO_2Me)CHC=CPh(C≡CCO_2-Me)}(PPh_3)Cp* **5**, showing the atom numbering scheme.

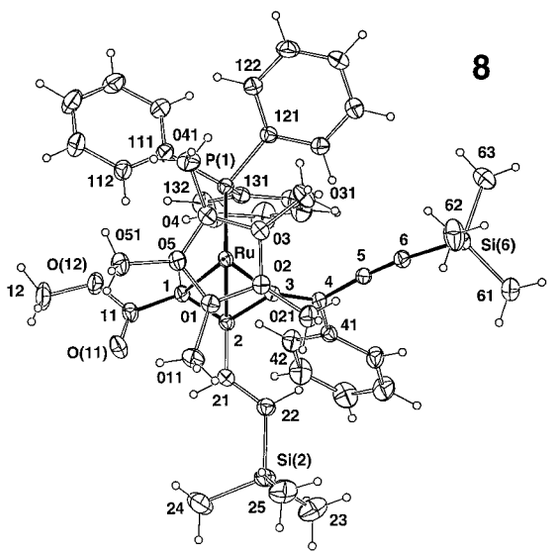


Fig. 4 Plot of a molecule of Ru{η^3-CH(CO_2Me)C(CH=CHSiMe_3)-C=CPhC≡CSiMe_3}(PPh_3)Cp* **8**, showing the atom numbering scheme.

with average values 2.234–2.290 Å [neglecting the values for **3**, which are commented upon below]. For example, in RuCl-(PPh_3)$_2$Cp* the average Ru–P distance is 2.341(6) Å, while Ru–C(Cp*) separations range between 2.224 and 2.274(2) Å.[14] The structure of complex **1** has been reported before for a different phase and our determination shows no significant differences from the earlier study.[6]

(a) Ru{η^1-C(C≡CPh)=CHC(O)OMe-*O*}(PPh_3)Cp* 3. In this complex two alkyne molecules have combined to form a five-membered chelate RuC_3O ring, C(2) forming a σ bond to the metal [Ru–C(2) 2.032(8) Å], while the ester carbonyl oxygen forms a donor bond [Ru–O(11) 2.156(5) Å]. Atoms C(3)–C(4) are separated by a triple bond, while C(1)–C(2) is a double bond. In this molecule both the Ru–P [2.281(3) Å] and average Ru–C(Cp*) separations [2.19$_2$ Å] are shorter than those found in the other five complexes, probably as a result of there being not only less steric interaction with the ring substituents, but also lack of back bonding into the organic ligand. The latter would result in more back donation into the PPh_3 and Cp* ligands with tighter bonding thereof.

(b) Ru{η^3-CH(CO_2Me)CHC=CPh(C≡CCO_2Me)}(PPh_3)Cp* 5 and Ru{η^3-CH(CO_2Me)C(CH=CHSiMe_3)C=CPhC≡CSi-Me_3}(PPh_3)Cp* 8. The structures of these two complexes are

Table 1 Selected bond parameters (bond lengths in Å, angles in °) for complexes **1**, **3** and **5**–**8**

	1[a]	**3**	**8**	**5**	**6**[a]	**7**[a]
Ru–P	2.311, 2.323(2)	2.281(3)	2.3322(9)	2.329(2)	2.335, 2.338(1)	2.330, 2.337(2)
Ru–C(Cp*)	2.220–2.256, 2.231–2.273(6)	2.178–2.224(9)	2.213–2.282(3)	2.203–2.274(5)	2.217–2.360, 2.231–2.372(6)	2.223–2.351, 2.208–2.368(7)
(av.)	2.23_6, 2.24_3	2.19_2	2.24_5	2.23_4	2.28_2, 2.29_0	2.28_1, 2.28_0
Ru–C(1)	2.305, 2.294(6)		2.214(3)	2.243(5)		
Ru–C(2)	2.124, 2.135(6)	2.032(8)	2.154(2)	2.117(5)	2.104, 2.098(4)	2.086, 2.087(5)
Ru–C(3)	2.029, 2.037(6)		2.044(3)	2.025(4)	2.066, 2.083(5)	2.072, 2.077(5)
Ru–C(6)					2.082, 2.085(5)	2.089, 2.096(5)
C(1)–C(2)	1.434, 1.426(9)	1.35(1)	1.425(5)	1.426(7)	1.337, 1.332(6)	1.344, 1.363(6)
C(1)–C(11)	1.448, 1.461(8)	1.44(1)	1.486(5)	1.470(8)	1.452, 1.465(6)	1.429, 1.439(7)
C(2)–C(3)	1.408, 1.421(8)	1.41(1)	1.419(4)	1.429(7)	1.342, 1.343(7)	1.339, 1.333(7)
C(3)–C(4)	1.339, 1.340(9)	1.19(1)	1.352(5)	1.349(6)	1.348, 1.337(7)	1.353, 1.343(8)
C(4)–C(5)	1.431, 1.439(9)		1.445(4)	1.456(8)	1.453, 1.456(7)	1.443(8), 1.455(7)
C(4)–C(41)	1.503, 1.494(9)	1.44(1)	1.485(3)	1.473(7)	1.472, 1.487(7)	1.461(9), 1.466(8)
C(5)–C(6)	1.193(9), 1.19(1)		1.202(5)	1.180(9)	1.348, 1.366(8)	1.338(9), 1.367(8)
C(6)–C(61)	1.448(9), 1.44(1)			1.441(9)	1.487, 1.486(7)	1.483(8), 1.460(7)
C(6)–O(61)					1.193, 1.183(7)	1.187, 1.189(7)
C(6)–O(62)					1.337, 1.347(7)	1.338, 1.299(7)
C(11)–O(11)		1.23(1)	1.196(4)	1.203(8)	1.197, 1.200(7)	1.203, 1.207(7)
C(11)–O(12)		1.36(1)	1.349(5)	1.353(7)	1.355, 1.356(7)	1.351, 1.348(6)
P–Ru–C,O(1)	83.7, 84.9(2)	87.7(2)	83.89(8)			
P–Ru–C(2)	106.7, 106.4(2)	90.3(2)	104.42(9)		88.8, 89.2(2)	89.2, 90.0(1)
P–Ru–C(3)	93.8, 93.5(2)		88.56(9)	92.0(2)	103.5, 103.7(1)	103.1, 104.8(2)
P–Ru–C(6)					89.5, 89.6(1)	88.3, 89.6(2)
C(2)–Ru–C(6)					108.2, 108.6(2)	108.4, 108.1(2)
C(3)–Ru–C(6)					74.0, 74.4(2)	74.0, 74.1(2)
C(11)–C(1)–C(2)	124.6, 124.8(5)	112.9(7)		119.7(5)	122.5, 122.3(4)	123.2, 121.6(5)
C(1)–C(2)–C(3)	119.6, 121.2(5)	118.8(7)	115.6(3)	115.6(5)	151.9, 150.9(5)	149.7, 151.6(5)
C(2)–C(3)–C(4)	134.1, 134.2(6)	177.7(8)	134.3(2)	131.2(5)	158.5, 160.6(5)	161.2, 161.3(5)
C(3)–C(4)–C(5)	120.6, 120.9(6)		121.8(2)	120.0(4)	109.8, 111.5(4)	109.9, 110.8(5)
C(3)–C(4)–C(41)	124.0, 123.3(6)	178.9(9)			126.8, 126.8(4)	
C(4)–C(5)–C(6)	176.6, 174.6(7)		175.2(3)		115.7, 114.8(4)	116.7, 115.2(5)
C(5)–C(6)–C(61)	176.3, 177.7(7)				115.7, 113.9(5)	117.1, 115.3(5)
C(1)–C(11)–O(11)		121.1(8)			127.5, 127.6(4)	127.4, 128.0(5)
C(1)–C(11)–O(12)		117.0(8)			110.3, 110.0(4)	111.2, 110.0(5)

[a] Values cited for molecule 1, 2. For **3**: Ru–O(11) 2.156(5), P–Ru–O(11) 87.7(2), O(11)–Ru–C(2) 77.0(3), Ru–O(11)–C(11) 112.2(6). For **5**: C(61)–O(61) 1.187(8), C(61)–O(62) 1.331(7). For **6**: C(6)–C(61)–O(61) 126.1(4), 125.9(5), C(6)–C(61)–O(62) 112.5, 112.5(4). For **7**: C(6)–C(61)–O(61) 125.8, 125.2(5), C(6)–C(61)–O(62) 111.9, 114.9(5). For **8**: C(2)–C(21) 1.485(4), C(21)–C(22) 1.329(6), Si(2)–C(22) 1.849(3), Si(6)–C(6) 1.830(4); Si(2)–C(22)–C(21) 125.9(3), C(3)–C(2)–C(21) 121.0(3), C(2)–C(21)–C(22) 126.8(3), Si(6)–C(6)–C(5) 173.8(3).

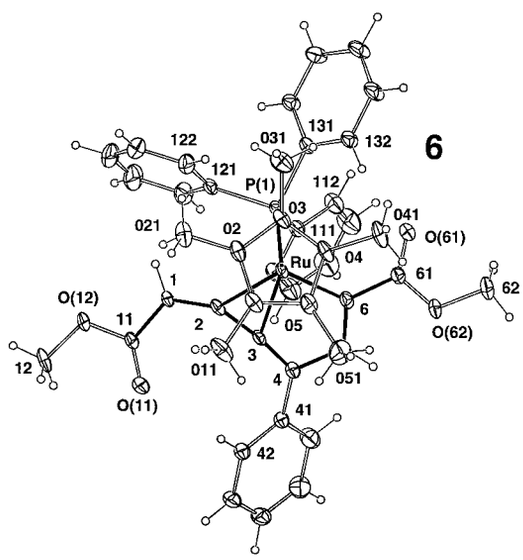


Fig. 5 Plot of a molecule of Ru{η^1,η^2-C(CO_2Me)=CHCPh=CC=CH(CO_2Me)}(PPh_3)Cp* **6**, showing the atom numbering scheme.

closely related to that of **1**, differing only in the substituents which, however, exert some influence on the geometrical parameters. Thus, an asymmetric allylic interaction of the ruthenium with atoms C(1,2,3) [Ru–C(1) 2.243(5), 2.214(3), Ru–C(2) 2.117(5), 2.154(2), Ru–C(3) 2.025(4), 2.044(3) Å] results from the presence of a double bond between C(3)–C(4) [1.349(6), 1.352(5) Å], *i.e.* the ligands are η^3-butadienyls. These data can be compared with those for **1**, in which the Ru–C and the C–C distances are consistent with the same arrangement of multiple bonds. In both **5** and **8**, atom C(1) carries H and CO_2Me substituents, while C(4) carries the phenyl and alkynyl groups. In **8** the central C(2) of the allyl also carries the *trans*-CH=CH($SiMe_3$) group [C(21)–C(22) 1.329(4) Å].

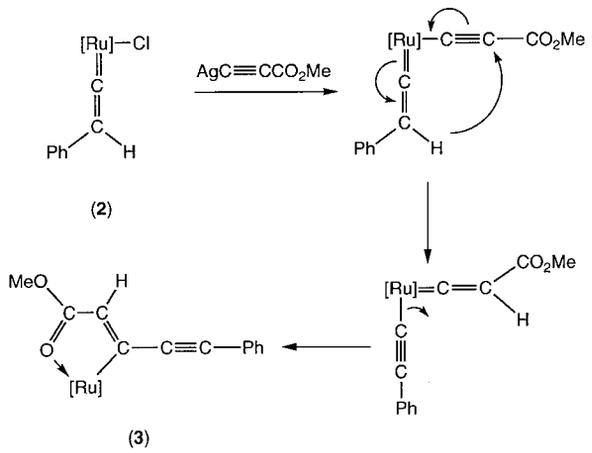
(c) Ru{η^1,η^2-C(CO_2R)=CHCPh=CC=CH(CO_2Me)}(PPh_3)-Cp* (R = Me 6 or Et 7). As expected, the molecular structures of complexes **6** and **7** are closely related and only **6** is depicted; the structural determination of **7** enables us to comment on the site of addition of the third alkyne molecule. The organic ligands in each of these complexes is a linear oligomer derived from three alkyne molecules and is attached to the ruthenium by a π bond to C(2)–C(3) [2.104(4), 2.066(5); 2.086(5), 2.072(5) Å; values for molecule 1 of each complex given] and a σ bond to C(6) [2.082(5); 2.089(5) Å]. Atoms C(1–4) form a cumulene, of which only the central C=C double bond is co-ordinated to ruthenium, while there is also a double bond between atoms C(5,6). The ligand is thus a 3-vinylbuta-1,2,3-triene, which is an isomer of the diene found in **5**. The substituents on atoms C(3,5,7) have normal geometries. There are close parallels between these structures and that of the complex Ru{η^1,η^2-C(CF_3)=CH(CF_3)=CC=CH(CF_3)}(PPh_3)Cp, another alkyne trimerisation product obtained from HC≡CCF_3 and RuH(PPh_3)$_2$Cp,[15] where, for example, the Ru–C distances are 2.11(1) (σ-bonded) and 2.05, 2.09(1) Å (π-bonded).

Discussion

Determination of the molecular structures of these complexes allows some comment on the likely mechanisms of their formation. In the earlier report on **1** it was suggested that trimerisation of the alkyne (HC≡CPh) occurred by initial co-ordination of phenylethyne to the alkynylruthenium centre as the phenylvinylidene, followed by dimerisation to intermediate **A**. Displacement of dimer by HC≡CPh with regeneration of the alkynylruthenium centre is followed by co-ordination of the dimer and intramolecular C–C bond formation occurs (formally insertion of the third alkyne into an Ru–C bond of the dimer; Scheme 1). Subsequent rearrangement involves co-ordination of the terminal olefinic bond to give **1**. This reaction course is encouraged by the steric bulk of the Cp* and PPh_3 ligands, which offer some stability to the postulated 16-e intermediates.

The first reaction we describe affords a product **3** which contains a ligand formed by formal combination of the phenylethynyl group with the ester vinylidene in precursor complex **4**. The same complex is formed in the reverse reaction, namely between **2** and $AgC{\equiv}CCO_2Me$. These results can be explained if replacement of the chloride in **2** is followed by a proton shift from the phenylvinylidene to the methoxycarbonylethynyl group, followed by insertion of the resulting $C{=}CH(CO_2Me)$ ligand into the Ru–C(sp) bond. Further reaction is prevented by chelation of the ester carbonyl group into the vacant co-ordination site on the metal centre (Scheme 3). The formation of **1** in the reaction of **4** with phenylethyne in the presence of base suggests that the intermediate containing the $C{=}CH(CO_2Me)$ ligand is labile towards replacement by phenylvinylidene, consistent with previously observed reactivities of complexes containing these two ligands.

In the reaction between complex **2** and methyl propiolate in the presence of base we find specific formation of **5**, which has a structure analogous to that of **1**, but with the terminal Ph groups replaced by CO_2Me, suggesting that in this case, dimerisation of the alkyne does not occur before complexation to the metal. We suggest that the first step in this reaction is replacement of chloride by the methyl propiolato group. Isomerisation of the phenylvinylidene to η^2-phenylethyne and insertion into the Ru–C(sp) bond gives co-ordinatively unsaturated intermediate **B**. Addition of a second molecule of methyl propiolate as its vinylidene isomer is followed by insertion into the Ru–$C(sp^2)$ bond, H migration and co-ordination of the terminal C=C double bond, as suggested for **1** (Scheme 4). Indeed, the

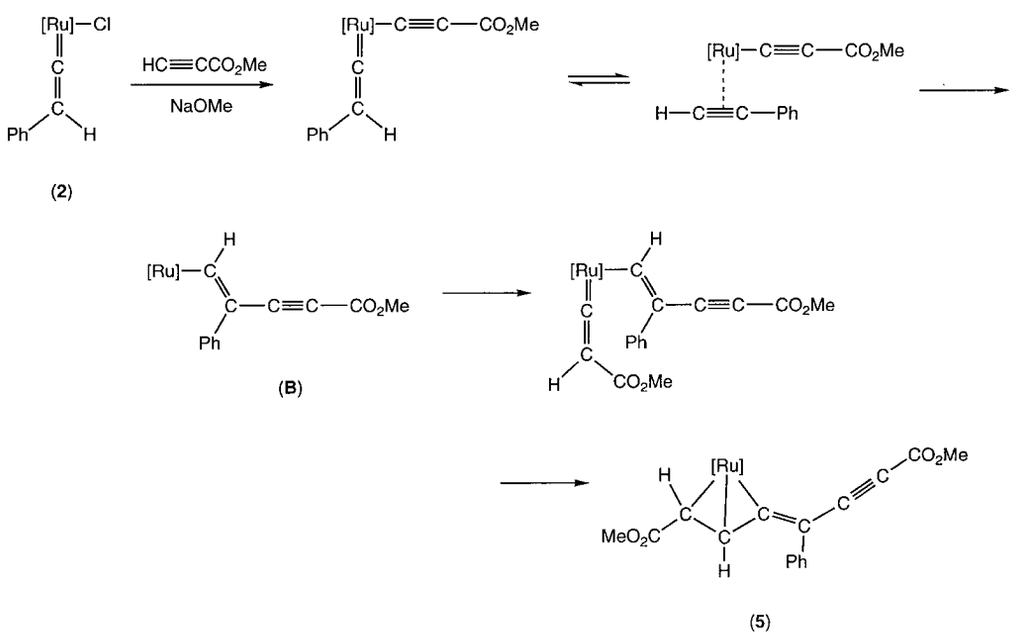


Scheme 3

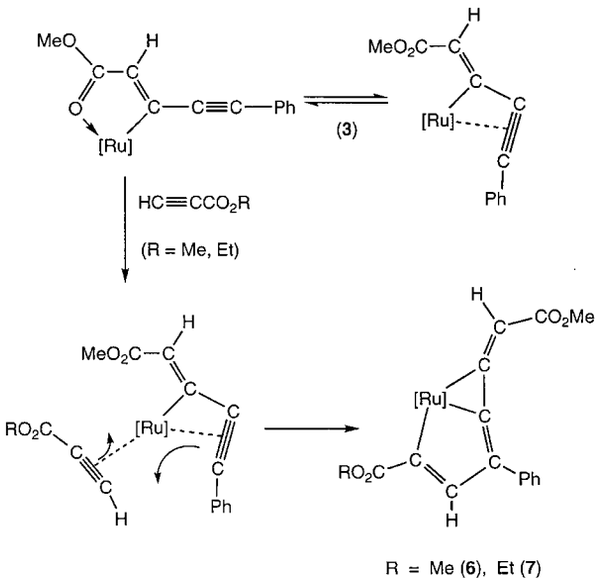
formation of **1** from **2** and HC≡CPh can also be described by an analogous sequence of reactions, which has the advantage of not requiring the formation of the alkyne dimer.

In an attempt to determine whether complex **3** is an intermediate en route to **5** we treated it with alkyl propiolates (methyl and ethyl). From these reactions we obtained complexes **6** and **7**, which were shown to contain cumulene ligands formed by addition of the alkyl ester to the "dimeric" ligand in **3**. The site of addition, defined as that closest to the metal centre by the presence of methyl or ethyl ester groups, respectively, can be accounted for if **3** isomerises to the η^2-alkyne isomer by displacement of the ester carbonyl group. This may require the presence of the alkyl propiolate, which can co-ordinate to the metal centre and couple to the Ph end of the co-ordinated C≡C triple bond (Scheme 5). We note that the organic ligand in these complexes is isomeric to that in **5**, which may be explained by a proton shift analogous to that found in conventional alkyne–allene rearrangements. Formulation of **6** and **7** as shown emphasises the metallacyclopentadiene structure, a familiar product or intermediate in alkyne oligomerisation reactions.

The reaction between **3** and $HC{\equiv}CSiMe_3$ gave an unprecedented type of complex containing a ligand derived from four alkyne molecules. In this case we suggest that isomerisation of **3** and addition of the free alkyne affords an η^2-alkyne intermedi-



Scheme 4



Scheme 5

ate similar to that shown in Scheme 5, which then undergoes an internal oxidative addition to the metal centre to give hydrido–alkynyl intermediate **C**. This is followed by coupling of the alkynyl and η^2-alkyne moieties, insertion of a second molecule of $HC{\equiv}CSiMe_3$ into the Ru–H bond of **C**, followed by coupling of the resulting vinyl with the terminal vinyl moiety to afford **8** (Scheme 6).

Conclusion

This work has demonstrated a novel series of stepwise reactions of alkynes with the neutral ruthenium vinylidene complexes $RuCl(=C{=}CHR)(PPh_3)Cp^*$ which result in a series of complexes containing ligands derived from between two and four alkyne molecules. Direct trimerisation or cyclotrimerisation of alkynes does not occur. Instead, individual steps involving single coupling of two alkyne-derived ligands are involved. These reactions appear to proceed by stepwise insertions of the alkyne into Ru–C σ bonds or by coupling of two alkynes at the ruthenium centre. In some cases, isomerisation of the alkyne to the corresponding vinylidene may precede these reactions. The mechanistic complexity of reactions of this type is further illustrated by the fact that the products described above are formed with a different regioselectivity from those obtained using *trans*-$RuCl_2(PPh_3)(pnp)$ [pnp = $NPr(C_2H_4PPh_2)_2$].[10] We have sought to demonstrate formation of possible intermediates by alternative syntheses, taking advantage of the presence of the chloride ligand in **2** and its ability to be replaced by alkynyl groups by means of reactions with alkali metal or silver derivatives of the alkynes, the latter being chosen to facilitate removal of chloride as insoluble AgCl.

Experimental

General reaction conditions

Reactions were carried out under an atmosphere of nitrogen, but no special precautions were taken to exclude oxygen during work-up. Common solvents were dried and distilled under nitrogen before use. Light petroleum refers to a fraction of bp range 60–80 °C. Elemental analyses were performed by the Canadian Microanalytical Service, Delta, B.C., Canada. Preparative TLC was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thickness).

Instrumentation

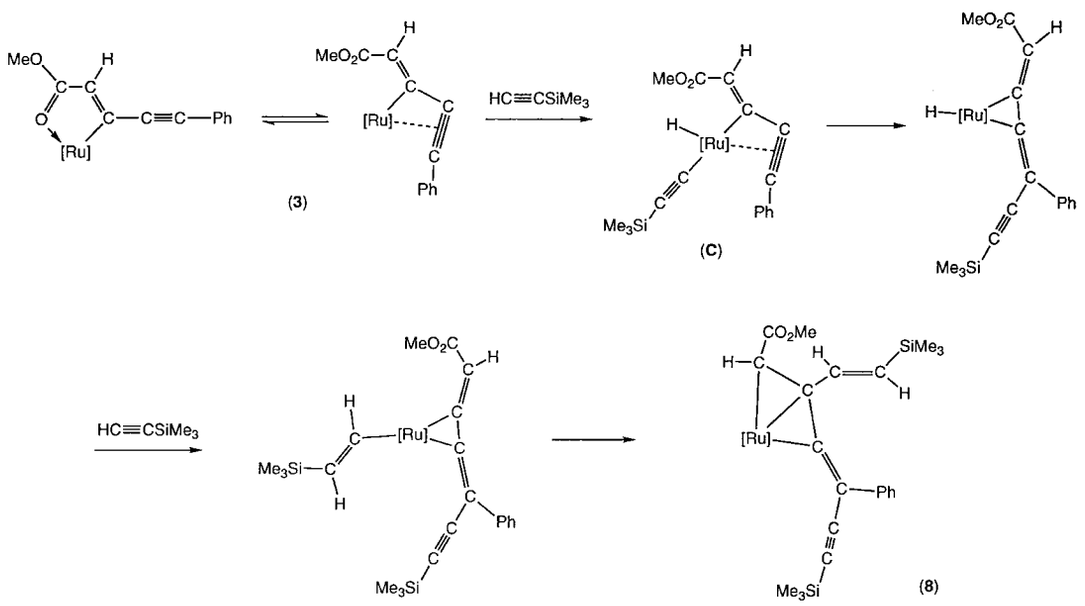
IR: Perkin-Elmer 1720X FT IR. NMR: Bruker CXP300 or ACP300 (^1H at 300.13 MHz, ^{13}C at 75.47 MHz) or Varian Gemini 200 (^1H at 199.8 MHz, ^{13}C at 50.29 MHz) spectrometers. Unless otherwise stated, spectra were recorded using solutions in $CDCl_3$ in 5 mm sample tubes. FAB mass spectra: VG ZAB 2HF (using 3-nitrobenzyl alcohol as matrix, exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7 kV). ES mass spectra: Finnegan LCQ. Solutions were directly infused into the instrument. Chemical aids to ionisation were used as required.[16]

Reagents

$RuCl(PPh_3)_2Cp^*$,[2] $RuCl(=C{=}CHPh)(PPh_3)Cp^*$,[1] and $RuCl\{=C{=}CH(CO_2Me)\}(PPh_3)Cp^*$[7] were prepared by literature methods; $HC{\equiv}CCO_2R$ (R = Me or Et) was obtained by esterification of propiolic acid (Aldrich).

Reactions of $RuCl(=C{=}CHPh)(PPh_3)Cp^*$ 2

(a) With HC≡CPh/NaOMe. A mixture of $RuCl(=C{=}CHPh)(PPh_3)Cp^*$ (100 mg, 0.157 mmol) and HC≡CPh (32 mg, 0.314 mmol) in MeOH (20 ml) was treated with an excess of NaOMe



Scheme 6

[from Na (0.92 g) in MeOH (2 ml)], after which the solution slowly changed from red to yellow. Cooling (0 °C) gave a yellow precipitate of Ru{η³-PhCHCHC=CPh(C≡CPh)}(PPh₃)Cp* **1** (84 mg, 67%). Found: C, 77.30; H, 5.89. Calc. for $C_{52}H_{47}PRu$: C, 77.68; H, 5.85%. IR (Nujol): ν(CC) 2181 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.36 [d, J(HP) 1.4, 15 H, Cp*], 3.02 [dd, J(HH) 9, J(HP) 14, 1 H, =CH], 3.38 [dd, J(HH) 9, J(HP) 3.7 Hz, 1 H, =CH] and 6.98–7.69 (m, 30 H, Ph). ^{13}C NMR ($CDCl_3$): δ 9.76 (s, $C_5\mathit{Me}_5$), 86.21 (s, ≡*C*Ph), 92.12 (s, C_5Me_5), 95.42 (s, C*C*Ph), 124.0–131.0 (m, Ph), 96.3, 114.00, 192.50 (C_3 chain). FAB mass spectrum (*m*/*z*): 804, M$^+$; 727, [M − Ph]$^+$; 679, [M − C_4Ph ?]$^+$; 601, [Ru(CCPh)(PPh₃)Cp*]$^+$; 542, [M − PPh₃]$^+$; 499, [Ru(PPh₃)Cp*]$^+$. Selected lit. values:[6] ^{1}H NMR δ 1.36 (s, Cp*), 3.00 [dd, J(HH) 8, J(HP) 14, =CH], 3.68 [dd, J(HH) 8.8, J(HP) 3.7 Hz, CH] and 7.0–7.8 (m, Ph); ^{13}C NMR δ 10.8 ($C_5\mathit{Me}_5$), 93.4 (C_5Me_5), 96.4, 114.8, 125.3, 192.6 (carbon chain).

(b) With LiC≡CPh. LiC≡CPh (24 mg, 0.24 mmol) in thf (2 ml) was added to RuCl(=C=CHPh)(PPh₃)Cp* (100 mg, 0.162 mmol) in the same solvent (10 ml) cooled to −55 °C. After warming to r.t. and stirring for 1 h, evaporation and chromatography of the residue (alumina column) afforded complex **1** (30 mg, 24%). A similar reaction between RuCl(=C=CHPh)(PPh₃)Cp* (200 mg, 0.324 mmol) and LiC≡CPh (70 mg, 0.64 mmol) in thf (20 ml) was treated by preparative TLC (acetone–hexane 1:4) to give **1** (64 mg, 26%).

(c) With silver methyl propiolate. A solution of RuCl(=C=CHPh)(PPh₃)Cp* (300 mg, 0.48 mmol) in thf (30 ml) was treated with AgC≡CCO_2Me (92 mg, 0.48 mmol) and the mixture stirred at r.t. for 2 h. The filtered solution (alumina) was evaporated and an acetone extract separated by preparative TLC to give recovered RuCl(=C=CHPh)(PPh₃)Cp* (12 mg, 4%) and Ru{η¹-C(C≡CPh)=CHC(O)OMe-*O*}(PPh₃)Cp* **3** (180 mg, 56%). X-Ray quality crystals were obtained from pentane. Found: C, 70.18; H, 5.85. Calc. for $C_{40}H_{39}O_2PRu$: C, 70.28; H, 5.71%. IR (cyclohexane): ν(C≡C) 2163w, ν(CO) 1724m, ν(C=C) 1558m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.40 [d, J(HP) 1.2, 15 H, Cp*], 3.33 (s, 3 H, CO_2Me), 6.25 [d, J(HP) 3.2 Hz, 1 H, CH] and 7.17–7.50 (m, 20 H, Ph). ^{13}C NMR ($CDCl_3$): δ 10.82 (s, $C_5\mathit{Me}_5$), 52.80 (s, OMe), 86.99 (s, C_5Me_5), 99.05, 100.57 (2 × s, ≡C), 122.97 (s, CH), 127.16–137.17 (m, Ph) and 181.26 (s, CO_2Me). ES mass spectrum (MeOH, *m*/*z*): 683, [M − H]$^+$; 499, [Ru(PPh₃)Cp]$^+$; 422, [Ru(PPh₂)Cp*]$^+$.

(d) With methyl propiolate and sodium methoxide. An excess of NaOMe was added to a solution of RuCl(=C=CHPh)(PPh₃)Cp* (100 mg, 0.16 mmol) and HC≡CCO_2Me (40 mg, 0.48 mmol) in MeOH (30 ml). After removal of solvent, the residue was separated by preparative TLC (acetone–hexane 1:4) into several bands. The major product was in a bright yellow band (R_f 0.50) which gave Ru{η³-CH(CO_2Me)CHC=CPh(C≡CCO_2Me)}(PPh₃)Cp* **5** (69.6 mg, 58%) as yellow crystals (CH_2Cl_2–EtOH). Found: C, 68.60; H, 5.52. Calc. for $C_{44}H_{43}O_4PRu$: C, 68.84; H, 5.61%. IR (cyclohexane): ν(C≡C) 2186m, ν(CO_2Me) 1706s, ν(C=C) 1616w, 1594w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.47 [d, J(HP) 1.4, 15 H, Cp*], 2.27 [dd, J(HH) 7.8, J(HP) 14.7, 1 H, CH], 3.59 [dd, J(HH) 7.8, J(HP) 3.8, 1 H, CH], 3.70, 3.94 (2 × s, 2 × 3 H, CO_2Me) and 7.04–7.35 (m, 20 H, Ph). ^{13}C NMR ($CDCl_3$): δ 9.16 [d, J(CP) 8.5, $C_5\mathit{Me}_5$], 50.52, 52.32 (2 × s, $CO_2\mathit{Me}$), 79.43, 94.05 (2 × s, C≡C), 93.67 (s, C_5Me_5), 124.58–139.33 (m, Ph), 112.11, 139.33, 155.55, 174.73 (C_4 chain) and 217.0 (s, $\mathit{C}O_2$Me). ES mass spectrum (MeOH + NaOMe, *m*/*z*): 791, [M + Na]$^+$; 767, [M − H]$^+$; 736, [M − H − OMe]$^+$. A brown band (R_f 0.58) contained complex **3** (5.7 mg, 5.3%).

Reactions of RuCl{=C=CH(CO_2Me)}(PPh₃)Cp* 4

(a) With silver phenylacetylide. Silver phenylacetylide (188 mg, 0.9 mmol) was added to a solution of RuCl{=C=CH(CO_2Me)}(PPh₃)Cp* (365 mg, 0.6 mmol) in thf (40 ml). After stirring for 4 h at r.t. in the dark, the red solution was filtered through alumina, evaporated *in vacuo* and an acetone extract of the residue purified by preparative TLC (acetone–hexane 1:4). The major brown band (R_f 0.58) was extracted with acetone and gave Ru{η¹-C(C≡CPh)=CHC(O)OMe-*O*}(PPh₃)Cp* **3** as a red-brown solid (288 mg, 71%), identified by comparison with the compound prepared as above.

(b) With ethynylbenzene and sodium methoxide. A solution of RuCl{=C=CH(CO_2Me)}(PPh₃)Cp* (62 mg, 0.1 mmol) and HC≡CPh (30 mg, 0.3 mmol) in MeOH (7 ml) was treated with a slight excess of NaOMe and stirred for 30 min at r.t., after which time starting complex **4** was no longer present (TLC). After removal of solvent, the residue was separated (TLC, acetone–hexane 1:4) into four fractions, all containing small amounts of material. Products from the bands with R_f 0.58 and 0.46 were identified as **3** (5 mg, 18%) and **1** (15 mg, 18%), respectively.

Reactions of Ru{η¹-C(C≡CPh)=CHC(O)OMe-*O*}(PPh₃)Cp* 3

(a) With methyl propiolate. A mixture of Ru{η¹-C(C≡CPh)=CHC(O)OMe-*O*}(PPh₃)Cp* (38 mg, 0.06 mmol) and HC≡CCO_2Me (10 mg, 0.12 mmol) was heated in refluxing hexane (20 ml) for 3 h. Separation of the major product by preparative TLC afforded Ru{η¹,η²-C(CO_2Me)=CHCPh=C=C=CH(CO_2Me)}(PPh₃)Cp* **6** (38.2 mg, 89%), contained in the red band (R_f 0.57). Dark red crystals were obtained from CH_2Cl_2–MeOH. Found: C, 68.66; H, 5.77. Calc. for $C_{44}H_{43}O_4PRu$: C, 68.84; H, 5.61%. IR (cyclohexane): ν(C≡C) 1953w, ν(CO) 1781m, 1723m, 1690s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.56 [d, J(HP) 1.2, 15 H, Cp*], 3.29, 3.33 (2 × s, 2 × 3 H, CO_2Me), 4.49 [d, J(HP) 1.5, 1 H, CH], 6.92–7.51 (m, 20 H, Ph) and 7.80 [d, J(HP) 3.8 Hz, 1 H, CH]. ES mass spectrum (MeOH + NaOMe, *m*/*z*): 791, [M + Na]$^+$; 775, [M + Na − O]$^+$; 691, [M − Ph]$^+$; 506, [M − PPh₃]$^+$; 499, [Ru(PPh₂)Cp*]$^+$.

(b) With ethyl propiolate. A similar reaction to (*a*), using Ru{η¹-C(C≡CPh)=CHC(O)OMe-*O*}(PPh₃)Cp* (50 mg, 0.07 mmol) and HC≡CCO_2Et (14 mg, 0.4 mmol), gave Ru{η¹,η²-C(CO_2Et)=CHCPh=C=C=CH(CO_2Me)}(PPh₃)Cp* **7** (41 mg, 72%) as red crystals (from CH_2Cl_2–MeOH). Found: C, 68.83; H, 5.88. Calc. for $C_{45}H_{45}O_4PRu$: C, 69.14; H, 5.76%. IR (cyclohexane): ν(CO) 1787m, 1699s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.01 (m, 3 H, Me), 1.52 [d, J(HP) 1.6, 15 H, Cp*], 3.37 (s, 3 H, CO_2Me), 3.61 (m, 2 H, OCH_2), 4.36 [d, J(HP) 3, 1 H, CH], 6.92–7.52 (m, 20 H, Ph) and 7.69 [d, J(HP) 3.4 Hz, 1 H, CH]. ES mass spectrum (MeOH + NaOMe, *m*/*z*): 805, [M + Na]$^+$; 781, [M − H]$^+$.

(c) With ethynyltrimethylsilane. A mixture of Ru{η¹-C(C≡CPh)=CHC(O)OMe-*O*}(PPh₃)Cp* (135 mg, 0.2 mmol) and ethynyltrimethylsilane (120 mg, 0.6 mmol) was heated in refluxing hexane (30 ml) for 2 h, after which the solution had changed from red to dark yellow. Two products were separated by preparative TLC (acetone–hexane 1:4). The first bright yellow band (R_f 0.76) contained Ru{η³-CH(CO_2Me)C(CH=CHSiMe₃)C=CPhC≡CSiMe₃}(PPh₃)Cp* **8** (21 mg, 12%), obtained as yellow crystals from hexane. Found: C, 67.89; H, 7.09. Calc. for $C_{50}H_{59}O_2PRuSi_2$: C, 68.26; H, 6.71%. IR (cyclohexane): ν(C≡C) 2115m, ν(CO) 1699s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ −0.23, 0.46 (2 × s, 2 × 9H, $SiMe_3$), 1.47 [d, J(HP) 1.2, 15 H, Cp*], 3.59 (s, 3 H, CO_2Me), 5.46 [d, J(HH) 18.9, 1 H, CH], 6.66 [d, J(HH) 18.9 Hz, 1 H, CH] and 6.59–7.26 (m, 21 H, Ph + CH). ES mass spectrum (MeOH, *m*/*z*): 880, M$^+$; 618, [M − PPh₃]$^+$; 603, [M − PPh₃ − Me]$^+$; 547, [M − PPh₃ − $SiMe_3$]$^+$. The second product was contained in a yellow band (R_f 0.64) and obtained as a yellow oil, unstable towards chromatography and in solution. This was tentatively identified as Ru{η³-CH(CO_2Me)CHC=CPh(C≡C$SiMe_3$)}(PPh₃)Cp* **9**. IR (cyclohexane):

Table 2 Crystal data and refinement details for complexes **1**, **3**, **5**, **6**, **7** and **8**

Compound	**1**	**3**	**5**	**6**	**7**	**8**
Formula	$C_{52}H_{47}PRu$	$C_{40}H_{39}O_2PRu\cdot 0.5C_5H_{12}$	$C_{44}H_{43}O_4PRu$	$C_{44}H_{43}O_4PRu$	$C_{45}H_{45}O_4PRu$	$C_{50}H_{59}O_2PRuSi_2\cdot C_6H_{12}$
M	804.0	719.9	767.9	767.9	781.9	966.4
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	10.386(4)	38.14(2)	18.013(6)	22.569(5)	22.793(16)	10.9167(8)
b/Å	20.927(6)	9.478(4)	10.666(5)	18.155(4)	18.423(19)	16.7444(11)
c/Å	37.598(14)	21.88(2)	10.382(2)	9.376(3)	9.378(7)	16.9819(12)
α/°			108.41(3)	76.66(2)	76.63(7)	63.452(1)
β/°	90.31(3)	109.66(7)	95.62(3)	83.89(2)	83.96(6)	78.627(1)
γ/°			91.70(3)	84.74(2)	84.66(7)	84.008(1)
V/Å^3	8172	7500	1880	3708	3800	$2721._9$
Z	8	8	2	4	4	2
D_c/g cm^{-3}	1.30_7	1.27_5	1.35_6	1.37_5	1.36_6	1.17_9
Crystal size/mm	0.65 × 0.10 × 0.19	0.15 × 0.28 × 0.25	0.35 × 0.22 × 0.10	0.14 × 0.35 × 1.00	0.19 × 0.23 × 0.80	0.50 × 0.38 × 0.16
A^* (min., max.)	1.04, 1.08	1.07, 1.14	1.05, 1.12	1.06, 1.19	1.07, 1.18	1.16, 1.32
μ/cm^{-1}	4.6	4.9	5.0	5.1	5.0	4.0
$2\theta_{max}$/°	50	50	50	55	50	58
N_{tot}		13704		29528	26629	31670
$N(R_{int})$	14096	6593 (0.060)	6613	16979 (0.054)	13344 (0.048)	13266 (0.026)
N_o	8357	237?	4988	11325	8094	9394
R	0.052	0.046	0.049	0.060	0.048	0.041
R_w	0.052	0.050	0.053	0.073	0.056	0.050
$\lvert\Delta\rho_{max}\rvert$/e Å^{-3}	0.9	0.43	1.1	1.9	1.4	0.65(2)

ν(C≡C) 2144w, ν(CO) 1707m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ −0.74 (s, 9 H, $SiMe_3$), 1.66 (s, 15 H, Cp*), 3.53 (s, 3 H, CO_2Me) and 6.71–7.83 (m, 20 H, Ph). ES mass spectrum (MeOH + NaOMe, m/z): 805, $[M + Na]^+$; 782, M^+; 520, $[M - PPh_3]^+$; 505, $[M - PPh_3 - Me]^+$; 449, $[M - PPh_3 - SiMe_3]^+$.

Structure determinations

Room-temperature single counter diffractometer data sets (T *ca.* 295 K; 2θ–θ scan mode, $2\theta_{max}$ as specified; monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å) were measured to the specified level of redundancy, N_{total} reflections (where other than unique) being merged after gaussian absorption correction, to N unique (R_{int} cited where appropriate), N_o with $I > 3\sigma(I)$ being used in the full matrix least squares refinement on $|F|$, minimising $\Sigma w\Delta^2$ and refining anisotropic thermal parameters for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimates. Conventional residuals R, R_w (statistical weights) are quoted at convergence. Neutral atom complex scattering factors were employed, computation using the XTAL 3.4 program system.[17] Pertinent results are given in Tables 1 and 2 and Figures, the latter showing 20% thermal ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. Individual variations in procedures, abnormalities, idiosyncrasies, *etc.*, are cited below.

Complex 3. Difference map residues are modelled as pentane solvate disordered about a crystallographic inversion centre, constrained geometry, isotropic carbon thermal parameter forms. A hemisphere of data was measured.

Complexes 6, 7. These are isomorphous and were refined in the same coordinate and cell setting. Full spheres of data were measured for both.

Complex 8. A full sphere of CCD area detector data was measured (Bruker AXS instrument, T *ca.* 300 K), 'empirical'/multiscan absorption correction being applied. Difference map residues were modelled as hexane, carbon thermal parameter forms isotropic, constrained geometries.

CCDC reference number 186/1965.

See http://www.rsc.org/suppdata/dt/b0/b001981j/ for crystallographic files in .cif format.

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