

Some reactions of allenylidene-ruthenium cluster carbonyls with alkynes

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Reactions of $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-CCPh}_2)(\mu\text{-OH})(\text{CO})_9$ (**1**) with alkynes and 1,3-diynes are described. With $\text{HC}\equiv\text{CSiMe}_3$, sequential formation of $\text{Ru}_3\{\mu_3\text{-CH}(\text{SiMe}_3)\text{CHCC}=\text{CPh}_2\}(\mu\text{-OH})(\text{CO})_9$ (**3**) and $\text{Ru}_3\{\mu_3\text{-Me}_3\text{SiCCHCHC}(\text{SiMe}_3)\text{-CC}=\text{CPh}_2\}(\text{CO})_8$ (**4**) occurred, whereas with $\text{HC}\equiv\text{CPh}$, the two isomeric complexes $\text{Ru}_3(\mu_3\text{-CR'CR'CR'CR'CRCC}=\text{CPh}_2)(\text{CO})_8$ [$\text{R} = \text{Ph}, \text{H}$, (**5a**), $\text{R}' = \text{H}, \text{Ph}$ (**5b**)] were isolated. These are formed by insertion of the alkyne into an Ru-C bond, with migration of the cluster H atom to the organic ligand. For **5**, elimination of the OH group with one alkyne H atom gives water. The metallabenzene complex $\text{Ru}_3\{\mu_3\text{-(FcCCH)}_2\text{CC}=\text{CPh}_2\}(\text{CO})_9$ (**6**) was obtained from **1** and $\text{HC}\equiv\text{CFc}$. The allenyl cluster $\text{Ru}_3\{\mu_3\text{-Ph}_2\text{CCC}(\text{CPh}=\text{CHPh})\}(\mu\text{-OH})(\text{CO})_9$ (**7**) is formed from **1** and $\text{PhC}\equiv\text{CPh}$. The allenyl complex $\text{Ru}_3\{\mu_3\text{-Me}_3\text{SiCC}(\text{C}=\text{CSiMe}_3)\text{CC}=\text{CPh}_2\}(\mu\text{-OH})(\text{CO})_9$ (**8**), formed from **1** and $\text{Me}_3\text{SiC}=\text{CC}=\text{CSiMe}_3$, and with a structure analogous to that of **3**, undergoes isomerisation on heating to yield $\text{Ru}_3\{\mu_3\text{-Ph}_2\text{CCCC}(\text{C}=\text{CSiMe}_3)=\text{CHSiMe}_3\}(\mu\text{-OH})(\text{CO})_9$ (**9**) by slippage of the organic ligand over the cluster. The reaction between **1** and $\text{FcC}\equiv\text{CC}=\text{CFc}$ affords $\text{Ru}_3\{\mu_3\text{-Ph}_2\text{CCCC}(\text{C}=\text{CFc})=\text{CHFc}\}(\mu\text{-OH})(\text{CO})_9$ (**10**), with a structure analogous to that of **9**.

Introduction

Metal complexes containing unsaturated carbene ligands continue to be a focus of contemporary chemistry.^{1,2} Although cluster complexes containing allenylidene ligands attached to Group 8 metal cluster carbonyl fragments have been known for nearly two decades,³ it is only recently that improved methods of synthesis^{4,5} have led to studies of their reactivity,^{6,7} the reactions between 1-alkynes and $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-CCPh}_2)(\mu\text{-OH})(\text{CO})_9$ (**1**) or $\text{Ru}_3(\mu_3\text{-CCPh}_2)(\mu\text{-CO})(\text{CO})_9$ (**2**) being of particular interest. Other examples of metal cluster complexes containing allenylidene ligands have been described.⁸⁻¹¹ This paper details our studies of the reactions of **1** with the alkynes $\text{HC}\equiv\text{CR}$ ($\text{R} = \text{SiMe}_3, \text{Ph}, \text{Fc}$), $\text{PhC}\equiv\text{CPh}$ and the 1,3-diynes $\text{RC}\equiv\text{CC}=\text{CR}$ ($\text{R} = \text{SiMe}_3, \text{Fc}$). The molecular structures of all complexes described have been determined by single-crystal X-ray studies.

Results

(a) Reactions of 1-alkynes

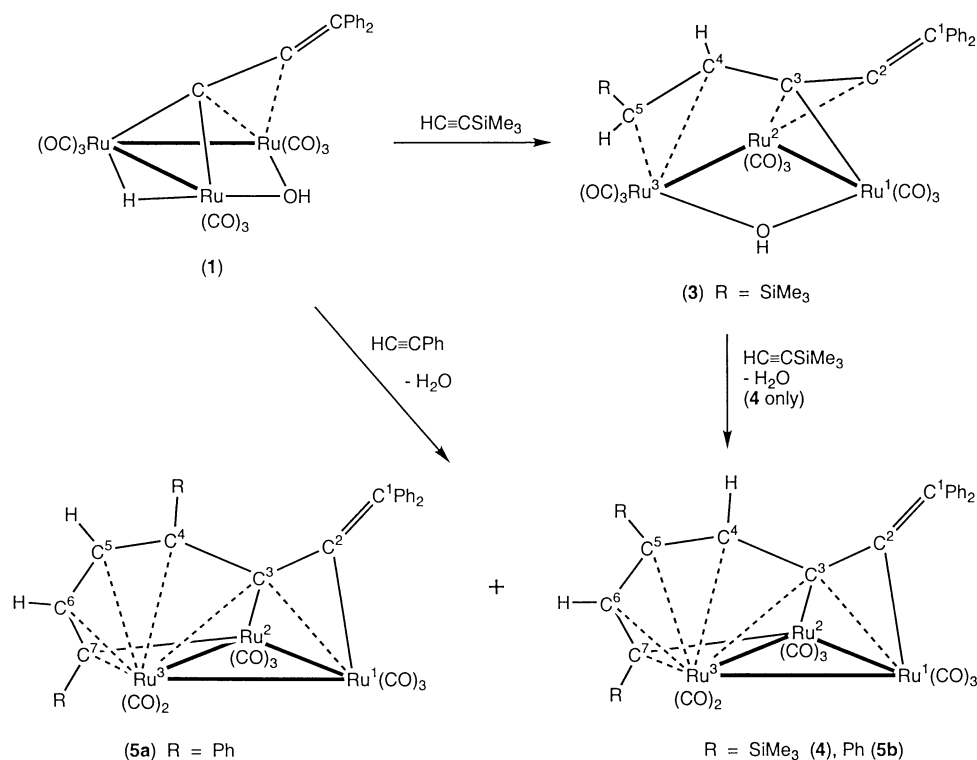
In contrast to the reactions of **2** with alkynes, which result in cluster fragmentation to give complexes containing isolated Ru and Ru_2 fragments or tetranuclear systems,⁵ all the reactions of **1** described below afford trinuclear clusters containing one or two molecules of the alkyne which have coupled with the diphenylallenylidene ligand. Thus, the reaction between **1** and $\text{HC}\equiv\text{CSiMe}_3$, carried out in dichloromethane at r.t., gave two complexes which were identified crystallographically as $\text{Ru}_3\{\mu_3\text{-CH}(\text{SiMe}_3)\text{CHCC}=\text{CPh}_2\}(\mu\text{-OH})(\text{CO})_9$ (**3**) and $\text{Ru}_3\{\mu_3\text{-Me}_3\text{SiCCHCHC}(\text{SiMe}_3)\text{CHCC}=\text{CPh}_2\}(\text{CO})_8$ (**4**) (Scheme 1). Subsequent experiments showed that **3** combines with another equivalent of the alkyne to give **4**, with simultaneous loss of the $\mu\text{-OH}$ group, in combination with one of the alkyne hydrogens, as water. In **3**, one molecule of the alkyne has combined with the Ph_2CCC ligand and the cluster-bound H atom to give a

5-substituted $\eta^1:\eta^2:\eta^2$ -1,1-diphenylpenta-1,2,4-triene ligand, in which the two coordinated double bonds are the 2,4-diene; C(3) is also attached *via* a σ bond to the third ruthenium. In **4**, the second molecule of alkyne couples in head-to-tail fashion to give a 4,6-disubstituted 1,1-diphenylhepta-1,2,4,6-tetraen-7-yl ligand, of which C(3) is attached to all three ruthenium atoms. With atom Ru(2), the resulting ligand forms a ruthenacyclohexadienyl ligand, attached in η^5 fashion to Ru(3) and bearing a vinyl substituent, which in turn interacts with the third Ru atom.

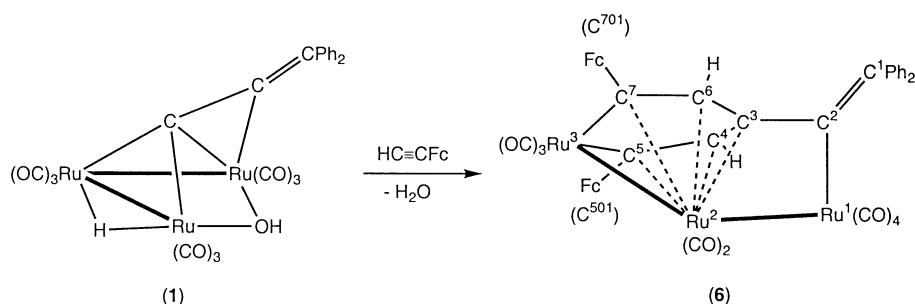
A similar reaction between **1** and $\text{HC}\equiv\text{CPh}$ gave two isomeric products, one of which (**5a**) was found to contain a ligand analogous to that in **4**, but in which the two alkyne molecules have coupled in head-to-head fashion, *i.e.* the two substituents are in the 5,7 positions. The similarity in spectral properties between the two isomers, and also of both with **4**, suggests that the second isomer (**5b**) is the head-to-tail coupled product. In this reaction, we did not find any evidence for the formation of the mono-alkyne derivative analogous to **3**.

Complexes **3**, **4** and **5a** were characterised by single-crystal X-ray structure determinations (see below), microanalytical and spectroscopic data being in accord with the solid-state structures. Thus, for **3**, the IR spectrum contains eight terminal $\nu(\text{CO})$ bands, together with a $\nu(\text{OH})$ absorption at 3620 cm^{-1} . The $^1\text{H NMR}$ spectrum contains an SiMe_3 singlet at δ 0.31 and an AB quartet for the two CH protons at δ 2.26 and 3.25; the OH resonance was not detected. The Ph multiplet is between δ 7.26 and 7.82. The electrospray (ES) mass spectrum (from methanol solution) contains the ions $[\text{M} + \text{MeOH} - n\text{CO}]^-$ ($n = 0-4$).

The IR spectra of **4**, **5a** and **5b** are similar, with seven terminal $\nu(\text{CO})$ bands between 2083 and 1953 cm^{-1} , but no $\nu(\text{OH})$ bands are present. In the $^1\text{H NMR}$ spectrum of **4**, there are two SiMe_3 singlets at δ 0.23 and 0.48, while the CH protons appear as singlets at δ 6.88 and 6.91. For **5a**, the latter signals are at δ 4.69 and 5.02, whereas in **5b**, an AB quartet at δ 6.37



Scheme 1



Scheme 2

and 6.63 is consistent with the proposed head-to-head linkage. The ES mass spectrum of **5b** contains $[\text{M} + \text{OMe}]^-$ at m/z 954.

The only tractable product (10%) from the reaction between **1** and $\text{HC}\equiv\text{CFc}$ was crystallographically identified as $\text{Ru}_3\{\mu_3\text{-}(\text{FcCCH})_2\text{CC}=\text{CPh}_2\}(\text{CO})_9$ (**6**; Scheme 2) and is formed by a double insertion of the alkyne into the Ru–C bonds of **1**. The resulting ligand is based on a ruthenacyclohexadienyl moiety, to the *para* carbon of which is attached a vinyl group derived from the original allenylidene. The IR $\nu(\text{CO})$ spectrum contains eight bands between 2097 and 1958 cm^{-1} , while the ^1H NMR spectrum contains singlet resonances for the Cp and CH protons at δ 3.85 and 5.31, respectively. Multiplets between δ 4.10 and 4.84, and between δ 6.96 and 7.49 are assigned to the C_5H_4 and Ph protons, respectively.

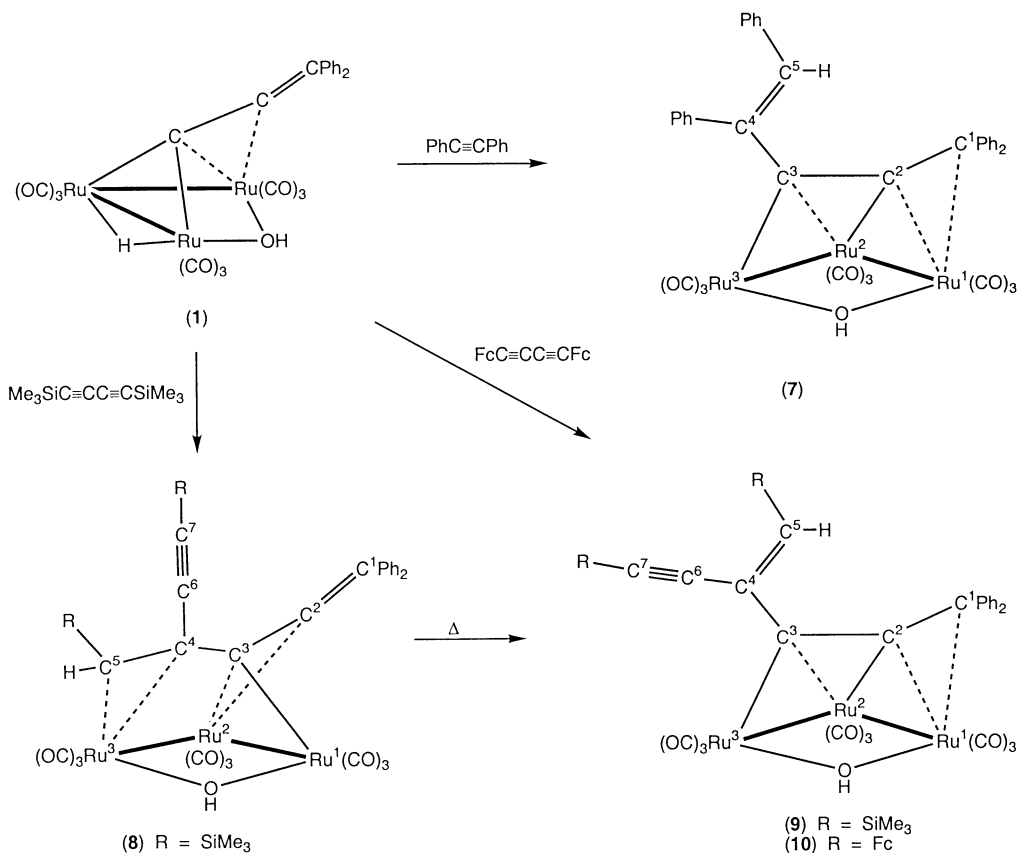
(b) Reaction of $\text{PhC}\equiv\text{CPh}$

A single product was obtained in 33% yield from the reaction between diphenylethyne and **1** and was characterised crystallographically as $\text{Ru}_3\{\mu_3\text{-Ph}_2\text{CCC}(\text{CPh}=\text{CHPh})\}(\mu\text{-OH})(\text{CO})_9$ (**7**) (Scheme 3). The organic ligand herein is best described as an $\eta^1:\eta^2:\eta^2$ -allenyl group, of which the 1,2-diphenylethenyl substituent has been formed by combination of the C_2Ph_2 and cluster-bound H atom with the allenylidene present in **1**. The IR spectrum contains six terminal $\nu(\text{CO})$ bands between 2088 and 1981 cm^{-1} and a $\nu(\text{OH})$ absorption at 3637 cm^{-1} . The

OH proton resonates at δ –5.31 (confirmed by its disappearance after addition of D_2O), while the CH singlet is found at δ 6.25.

(c) Reactions with 1,3-diynes

A r.t. reaction between **1** and $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$ afforded a single product in high yield, characterised as the vinylallenyl complex $\text{Ru}_3\{\mu_3\text{-Me}_3\text{SiCC}(\text{C}\equiv\text{CSiMe}_3)\text{CC}=\text{CPh}_2\}(\mu\text{-OH})(\text{CO})_9$ (**8**) by an X-ray structure determination (Scheme 3). The alkyne has formally inserted into one of the Ru–C σ bonds linking the allenylidene ligand to the cluster in concert with migration of the cluster-bonded hydrogen in **1** to C(5). On heating in refluxing dichloromethane for 30 min, quantitative isomerisation of **8** to $\text{Ru}_3\{\mu_3\text{-Ph}_2\text{CCCC}(\text{C}\equiv\text{CSiMe}_3)\text{-CHSiMe}_3\}(\mu\text{-OH})(\text{CO})_9$ (**9**) occurred by a formal slippage of the organic ligand along the Ru₃ cluster. For **8** and **9**, similar IR spectra with six terminal $\nu(\text{CO})$ bands between 2086 and 1984 cm^{-1} are found, together with $\nu(\text{OH})$ absorptions at 3629 and 3633 cm^{-1} , respectively. In their ^1H NMR spectra, two SiMe_3 singlets at δ –0.21, 0.48 (**8**), and at δ 0.00, 0.17 (**9**), are found, together with the CH singlets at δ 2.23 (**8**) and 6.38 (**9**), the latter in accord with the different environments of these protons. The OH resonance was found only for **9**, at δ –5.25. The highest m/z peak in the ES mass spectra (m/z 988 in both spectra) is assigned to $[\text{M} + \text{OMe} - 2\text{H}]^-$.



Scheme 3

Only one product was obtained pure from the similar reaction between **1** and $\text{FcC}\equiv\text{CC}\equiv\text{CFc}$, crystallographic characterisation of which showed it to be the analogue of **9**, namely $\text{Ru}_3\{\mu_3\text{-Ph}_2\text{CCCC}(\text{C}\equiv\text{CFc})=\text{CHFc}\}(\mu\text{-OH})(\text{CO})_9$ (**10**). Although several other complexes are formed in this reaction, including a possible precursor of **10** analogous to **8**, it has not been possible to identify any of them. For **10**, $\nu(\text{OH})$ is at 3632 cm^{-1} , while of the eight bands between 2093 and 1984 cm^{-1} in the $\nu(\text{CO})$ region, the highest energy band may be $\nu(\text{C}\equiv\text{C})$ from the uncoordinated $\text{C}\equiv\text{C}$ triple bond. Singlets for the two Cp rings and the CH protons occur at δ 4.05, 4.40 and 6.18, respectively, while multiplets for the C_5H_4 and Ph protons are found at 4.14–4.77, and at δ 7.13–7.80, respectively. The OH proton resonates at δ –5.49.

Molecular structures

(a) $\text{Ru}_3(\mu_3\text{-CHRCHCC}=\text{CPh}_2)(\mu\text{-OH})(\text{CO})_9$ (R = SiMe₃, **3**, **Ph 8**)

The molecular structures of complexes **3** and **8** are similar and can be conveniently discussed together here. Plots of single molecules of each complex are given in Fig. 1 and 2, respectively, and selected bond parameters for all complexes described here are collected in Table 1. The original hydroxy-bridged open Ru_3 core present in **1** is retained in both complexes [Ru–O 2.102(3)–2.146(7) Å], with normal Ru(1)–Ru(2) separations [2.760(1), 2.7407(4) Å for **3** and **8**, respectively] but rather long Ru(2)–Ru(3) bonds [3.007(1), 2.9756(4) Å]. In each case, the vinylallenyl ligand is attached to the cluster by a σ bond from C(3) to Ru(1) [2.07(1), 2.085(3) Å] and π bonds from C(2)–C(3) to Ru(2) [2.153–2.249(3) Å] and from C(4)–C(5) to Ru(3) [2.28(1)–2.327(3) Å]. The C–C separations along the C(1)–C(5) chains are consistent with a sequence of uncoordinated C=C [1.34, 1.329(5) Å], coordinated C=C [1.38, 1.394(5) Å], C–C single [1.47, 1.470(5) Å] and coordinated C=C [1.39, 1.408(5) Å] bonds.

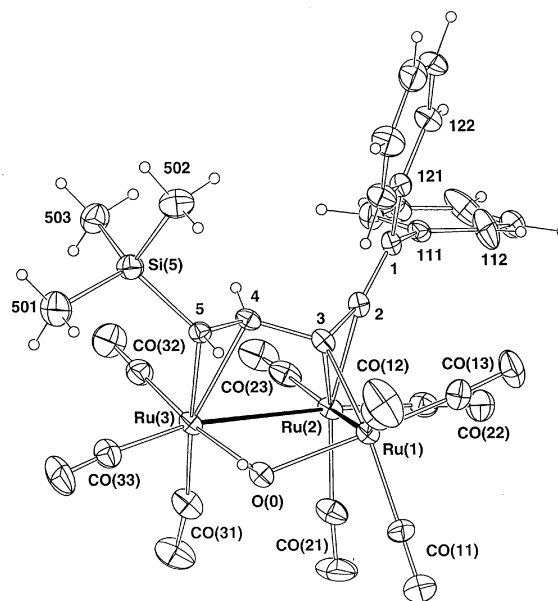


Fig. 1 Projection of a molecule of $\text{Ru}_3\{\mu_3\text{-CH}(\text{SiMe}_3)\text{CHCC}=\text{CPh}_2\}(\mu\text{-OH})(\text{CO})_9$ (**3**).

(b) $\text{Ru}_3(\mu_3\text{-CR'CR'CR'CC}=\text{CPh}_2)(\text{CO})_8$ (R = SiMe₃, R' = H; R = H, R' = Ph **5a**)

Fig. 3 and 4 are plots of individual molecules of the two complexes. As mentioned above, the structures found for **4** and **5a** are analogous and differ only in the position and nature of the substituents originally on the 1-alkynes. In both, a closed Ru_3 core supports a ligand formed by combination of the original allenylidene with two molecules of the alkyne. This forms a ruthenacyclohexadienyl by bonding to Ru(2) through two Ru–C σ bonds from C(3) and C(7) [2.055, 2.146(5) Å] (data for

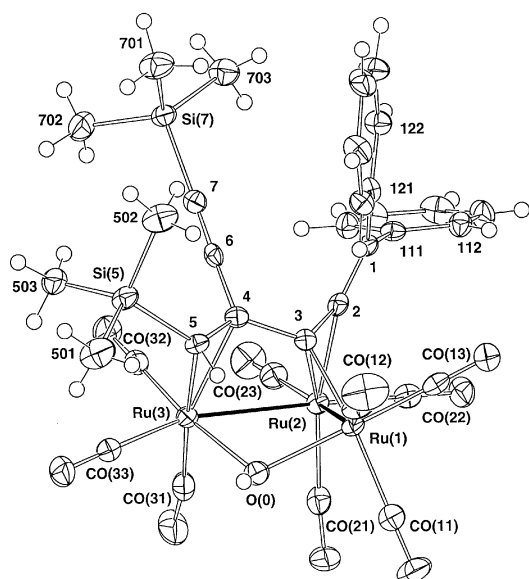


Fig. 2 Projection of a molecule of $\text{Ru}_3\{\mu_3\text{-Me}_3\text{SiCC}(\text{C}\equiv\text{CSiMe}_3)\text{CC}=\text{CPh}_2\}(\mu\text{-OH})(\text{CO})_8$ (**8**).

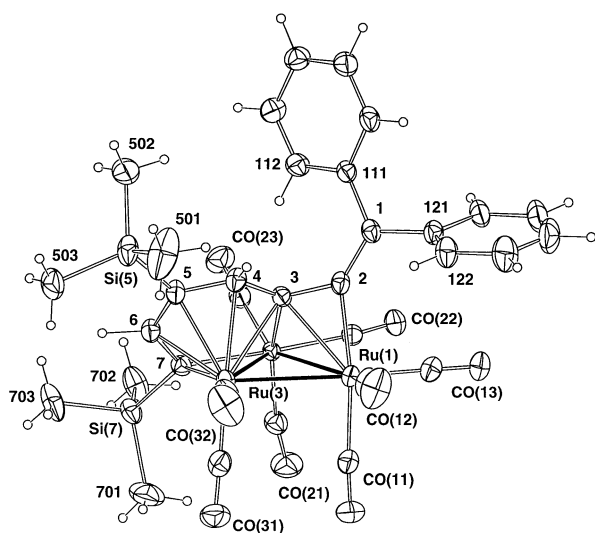


Fig. 3 Projection of a molecule of $\text{Ru}_3\{\mu_3\text{-Me}_3\text{SiCCHC}(\text{SiMe}_3)\text{CHCC}=\text{CPh}_2\}(\text{CO})_8$ (**4**).

4) and to Ru(3) by atoms C(3)–C(7) in an η^5 π -bonding mode [Ru–C 2.201–2.451(7) Å], while atom Ru(1) interacts with C(2) and C(3) as a rather asymmetric π bond [2.110(5), 2.421(6) Å]. Similar dimensions are found in **5a** (Table 1). The long Ru(1)–C(3) and Ru(3)–C(3) separations are probably the result of steric constraints rather than any well-defined electronic effect of the organic ligand. The pattern of substitution on C(4)–C(7) (**4**: H, SiMe₃, H, SiMe₃; **5a**: Ph, H, H, Ph) is consistent with head-to-tail coupling (in **4**) and head-to-head coupling of the two alkyne molecules (in **5a**). The approximately isosceles triangular Ru₃ cores have one long [2.860(2); 2.831, 2.846(2) Å] and two shorter [2.789, 2.775(2) for **4**, 2.799–2.802(2) Å for **5a**] Ru–Ru separations. The coordination of each ruthenium is completed by CO groups [three each on Ru(1) and Ru(2), two on Ru(3)] and the cluster has 48 c.v.e., with the organic ligand acting as an 8e[−] donor.

(c) $\text{Ru}_3\{\mu_3\text{-(FcCCH)}_2\text{CC}=\text{CPh}_2\}(\text{CO})_6$ **6**

Fig. 5 is a plot of a molecule of **6**. In contrast to **4** and **5a**, the three Ru atoms form a bent array [Ru(1)–Ru(2)–Ru(3) 158.17(1)^o] and the organic ligand has been formed by addition

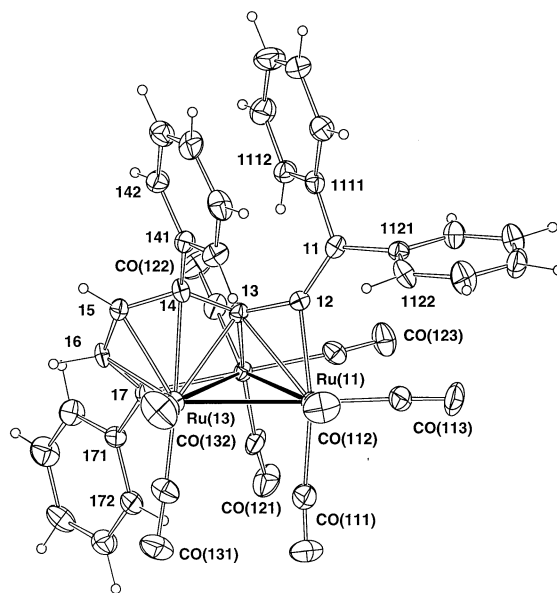


Fig. 4 Projection of a molecule of $\text{Ru}_3\{\mu_3\text{-PhCCHCHCPhCC}=\text{CPh}_2\}(\text{CO})_8$ (**5a**).

of two HC₂Fc units to the σ -bonded carbon of the allenyldiene in **1**, here denoted C(3). Of considerable interest is the interaction of this ligand with the three ruthenium atoms. Atom Ru(1) is weakly σ -bonded to C(2) [2.154(2) Å], while the six-membered metallabenzene ring is attached to Ru(2) in an η^5 mode from C(3)–C(7) [Ru–C 2.217–2.535(2) Å]. Atom Ru(3) forms part of the RuC₅ ring with two σ bonds to C(5) and C(7) [2.083, 2.054(2) Å]. The C(5)–Ru(3)–C(7) angle is 88.42(8)^o. Around the six-membered ring, C–C distances range between 1.407 and 1.437(3) Å, with angles at carbon between 120.8(0) and 128.4(0)^o; the C(5)–Ru(3)–Ru(7) angle is 88.42(8)^o, consistent with approximately octahedral coordination for this atom, which achieves an 18e[−] count with the four CO groups and the Ru(1)–Ru(2) bond. In contrast, atoms Ru(2) and Ru(3) are not electron-precise, the Ru(2)–Ru(3) bond being considered to be a 2e[−] donor bond in that direction.

(d) $\text{Ru}_3\{\mu_3\text{-Ph}_2\text{CCC}(\text{CPh}=\text{CHPh})\}(\mu\text{-OH})(\text{CO})_6$ **7 and $\text{Ru}_3\{\mu_3\text{-Ph}_2\text{CCCC}(\text{C}=\text{CR})=\text{CHR}\}(\mu\text{-OH})(\text{CO})_6$ (**R** = SiMe₃ **9**, Fc **10**)**

Fig. 6–8 contain plots of molecules of these three complexes. All three contain an open Ru₃ array [Ru(1)–Ru(2)–Ru(3) 76.06, 76.37 and 76.98(1)^o, respectively]. Atoms Ru(1) and Ru(3) are spanned by a hydroxy group [Ru–O 2.086–2.121(3) Å] while the organic ligand is attached to all three metal atoms by σ bonds from Ru(3) to C(3) [2.076, 2.052, 2.082(3) Å] and asymmetric π bonds from C(1)–C(2) to Ru(1) [2.220–2.244(3), 2.408–2.434(3) Å]. Short Ru(2)–C(2) separations [2.081–2.109(3) Å] are consistent with the presence of a σ bond, but atom C(3) is between 2.248 and 2.279(3) Å distant from Ru(2), suggesting either a weak σ bond, or a very asymmetric π bond to this atom from the C(2)–C(3) moiety.

The geometry of the bonded Ru₃C₃ fragment is similar to those found in $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-EtC}=\text{CHMe})(\text{CO})_9$,¹² $\text{Ru}_3(\mu_3\text{-Pr}^i\text{C}=\text{C}=\text{CH}_2)(\mu\text{-PPh}_2)(\text{CO})_8$,¹³ and $\text{Ru}_3(\mu_3\text{-Pr}^i\text{C}=\text{C}=\text{CH}_2)(\mu\text{-PPh}_2)(\mu\text{-CH}_2)(\text{CO})_7$,¹⁵ which have angles at the central carbon between 142.3(6) and 146.8(4)^o and those equivalent to Ru(3)–C(3)–C(2) of between 105.0(2) and 109.3(4)^o. While there are long Ru–Ru separations in the first two complexes [2.994(1) and 3.0965(7) Å, respectively], only in the hydrido cluster can this be related to the presence of the $\mu\text{-H}$ ligand. No similar lengthening is found in the $\mu\text{-CH}_2$ derivative. Also relevant to the present examples is the wide range of Ru–C distances found in the formally π -bonded interactions [2.089(5) to 2.341(6) Å]. Explanations for these observations are probably to be found in the above simplistic view of these com-

Table 1 Selected bond parameters for complexes **3**, **4**, **5a** and **6–10**

	3	4	5a (molecules 1, 2)	6^a	7	8	9	10^b
Bond distances/Å								
Ru(1)–Ru(2)	2.760(1)	2.789(1)	2.799(2), 2.790(1)	2.8317(3)	2.8262(4)	2.7407(4)	2.8396(5)	2.8191(6)
Ru(1)–Ru(3)		2.860(2)	2.831(2), 2.846(2)					
Ru(2)–Ru(3)	3.007(1)	2.775(1)	2.802(1), 2.783(2)	2.7478(3)	2.7867(4)	2.9756(4)	2.7886(4)	2.7806(6)
Ru(1)–O(0)	2.146(7)				2.086(2)	2.131(3)	2.089(2)	2.098(2)
Ru(3)–O(0)	2.117(7)				2.113(2)	2.102(3)	2.108(2)	2.121(3)
Ru(1)–C(1)					2.408(3)		2.431(3)	2.434(3)
Ru(1)–C(2)		2.110(5)	2.11(1), 2.12(1)	2.154(2)	2.244(3)		2.220(3)	2.228(3)
Ru(1)–C(3)	2.07(1)	2.421(6)	2.48(1), 2.447(8)			2.085(3)		
Ru(2)–C(2)	2.18(1)				2.099(3)	2.153(4)	2.081(3)	2.109(3)
Ru(2)–C(3)	2.22(1)	2.055(5)	2.06(1), 2.08(1)	2.217(2)	2.274(3)	2.249(4)	2.248(3)	2.279(3)
Ru(2)–C(7)		2.146(5)	2.11(1), 2.09(1)	2.535(2)				
Ru(3)–C(3)		2.451(4)	2.37(1), 2.41(1)		2.076(3)		2.052(3)	2.082(3)
Ru(3)–C(4)	2.28(1)	2.288(5)	2.31(1), 2.32(1)			2.327(4)		
Ru(3)–C(5)	2.29(1)	2.304(6)	2.28(1), 2.28(1)	2.083(2)		2.298(4)		
Ru(3)–C(6)		2.255(7)	2.27(1), 2.27(1)					
Ru(3)–C(7)		2.201(6)	2.25(1), 2.22(1)	2.054(2)				
Si(5)–C(5)	1.849(9)					1.893(4)	1.879(4)	
Si(7)–C(7)						1.850(4)	1.831(4)	
C(1)–C(2)	1.34(1)	1.348(6)	1.35(2), 1.35(2)	1.354(3)	1.396(3)	1.329(5)	1.395(4)	1.395(5)
C(2)–C(3)	1.38(1)	1.417(7)	1.43(2), 1.40(2)	1.480(3)	1.406(3)	1.394(5)	1.415(4)	1.397(5)
C(3)–C(4)	1.47(1)	1.436(6)	1.45(2), 1.45(2)	1.437(3)	1.499(4)	1.470(5)	1.507(4)	1.500(5)
C(4)–C(5)	1.39(1)	1.407(7)	1.41(2), 1.42(2)	1.411(3)	1.345(4)	1.408(5)	1.351(4)	1.348(5)
C(4)–C(6)						1.443(5)	1.439(4)	1.446(5)
C(5)–C(6)		1.425(7)	1.43(2), 1.40(2)					
C(6)–C(7)		1.410(7)	1.40(2), 1.44(2)	1.407(3)		1.207(5)	1.209(5)	1.195(5)
C(x)–C(x01)				1.491(2) [x = 5] 1.482(3) [x = 7]				1.445(5) [x = 5] 1.440(5) [x = 7]
Bond angles/°								
Ru(1)–Ru(2)–Ru(3)	75.49(3)	61.87(3)	60.71(4), 61.43(5)	158.17(1)	76.06(1)	75.49(1)	76.37(1)	76.98(1)
Ru(1)–O(0)–Ru(3)	112.1(3)				110.9(1)	111.8(1)	112.0(1)	111.4(1)
C(3)–Ru(2)–C(7)		89.6(2)	90.1(5), 90.6(6)					
C(1)–C(2)–C(3)	144(1)	133.7(6)	135(1), 136.7(9)	124.3(2)	137.6(3)	143.0(4)	133.9(3)	137.8(3)
C(2)–C(3)–C(4)	112.4(9)	116.0(4)	120(1), 120(1)	123.1(2)	117.3(2)	116.1(3)	114.6(2)	116.7(3)
C(2)–C(3)–C(6)				115.5(2)				
C(4)–C(3)–C(6)				120.8(2)				
C(4)–C(3)–Ru(2)		125.8(3)	127(1), 125(1)					
C(3)–C(4)–C(5)	129.2(9)	128.7(5)	125(1), 127(1)	127.0(2)	121.9(2)	124.3(3)	123.5(3)	120.8(3)
C(3)–C(4)–C(6)						117.0(3)	116.1(2)	118.0(3)
C(5)–C(4)–C(6)						117.7(3)	120.4(3)	
C(4)–C(5)–C(6)		122.1(4)	127(1), 126(1)					
C(4)–C(5)–Si(5)	122.0(7)					125.4(3)	124.9(3)	
C(4)–C(6)–C(7)						174.6(4)	178.1(3)	178.1(4)
C(5)–C(6)–C(7)		127.9(4)	126(1), 126(1)					
C(6)–C(7)–Si(7)						173.2(3)	176.8(3)	
Ru(2)–C(7)–C(6)		123.8(3)	124(1), 124(1)					

^a Additional data for **6**: Ru(2)–C(4) 2.278(2), Ru(2)–C(5) 2.451(2), Ru(2)–C(6) 2.313(2), C(3)–C(6) 1.421(3) Å; C(5)–Ru(3)–C(7) 88.42(8), C(4)–C(5)–Ru(3) 126.4(1), C(6)–C(7)–Ru(3) 126.2(1), C(2)–C(3)–C(6) 115.5(2), C(4)–C(3)–C(6) 120.8(2), C(3)–C(6)–C(7) 128.4(2)°. ^b Additional data for **10**: C(4)–C(5)–C(501) 130.5(3), C(6)–C(7)–C(701) 175.7(4)°.

pounds as metal clusters containing π -bonded ligands, whereas a more comprehensive view of the bonding (and hence the observed geometries) is obtained by considering them as C_3Ru_3 clusters. Even then, the MO levels can be perturbed by the presence of other bridging ligands, as has been well established for μ -phosphido complexes.¹⁴

Discussion

The reactions between alkynes and $Ru_3(\mu-H)(\mu_3-CCCPh_2)(\mu-OH)(CO)_2$, **1** afford complexes by formal insertion of the alkyne into one of the Ru–C σ bonds. In the case of $HC\equiv CSiMe_3$, the resulting five-carbon ligand is attached by means of one σ and two π bonds involving four out of the five carbons. Reaction with a second molecule of alkyne results in a second insertion, which may proceed in either of the two possible directions. For $HC\equiv CPh$, only the bis-insertion product was obtained, as a separable mixture of the head-to-head and head-to-tail isomers **5a** and **5b**. Complex **3** reacts with $HC\equiv CPh$ to give the mixed complex, although we were not able to determine the sites of substitution on the six-membered ring.

The bis-insertion product contains a seven-carbon ligand, of which the original allenylidene remains attached to Ru(1) *via* a π bond from C(2)–C(3). The two Ru–C interactions in the latter are unusually long and unusually short, with average separations of 2.265 (**4**) and 2.295 Å (**5a**). The remaining five carbons form an RuC_5 ring *via* two Ru–C σ bonds to Ru(2), which interacts further with Ru(3) by π -type bonds from C(3)–C(7). One of these is long, perhaps because of steric constraints resulting from the carbon atom [C(3)] interacting with all three ruthenium atoms.

A bis-insertion product with a different structure **6** is obtained from **1** and $HC\equiv CFc$, both molecules of alkyne inserting into one of the original Ru–C σ bonds in **1**. Thus a RuC_5 ring is formed, which interacts with Ru(2) *via* the five carbons. The central carbon, C(3) is part of the original $CCCPh_2$ ligand in **1**. In turn, this is attached to Ru(1) *via* an Ru–C σ bond. Migration of a CO group, presumably from Ru(2), has also occurred, to give an octahedral $Ru(CO)_4$ moiety. Simple electron counting gives formal 18-, 19- and 17e[−] counts to Ru(1), Ru(2) and Ru(3), respectively, the cluster having the anticipated 50 c.v.e. Formally, the Ru(2)–Ru(3) bond can be

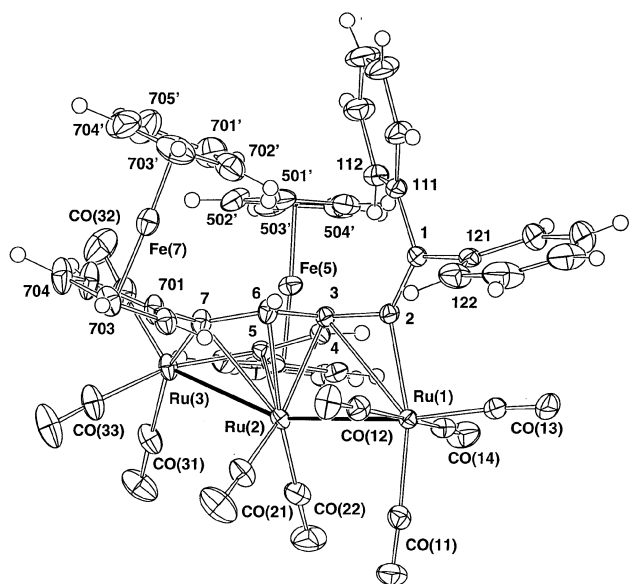


Fig. 5 Projection of a molecule of $\text{Ru}_3\{\mu_3\text{-(FcCCH)}_2\text{CC=CPh}_2\}\text{(CO)}_9$ (6).

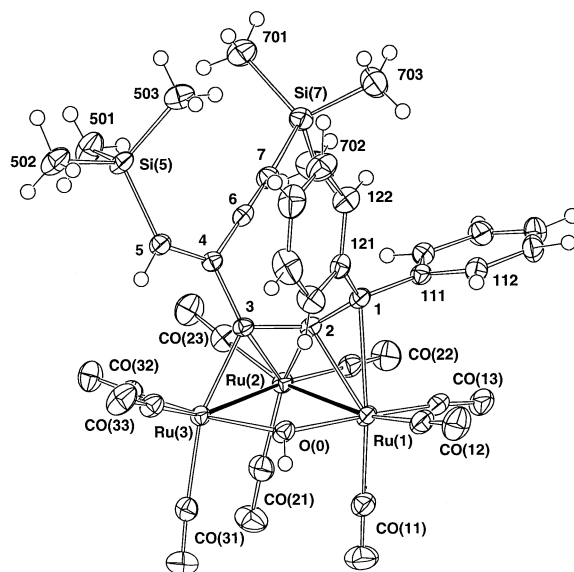


Fig. 7 Projection of a molecule of $\text{Ru}_3\{\mu_3\text{-Ph}_2\text{CCCC(C}\equiv\text{CSiMe}_3\text{)=CHSiMe}_3\}\text{(}\mu\text{-OH)(CO)}_9$ (9).

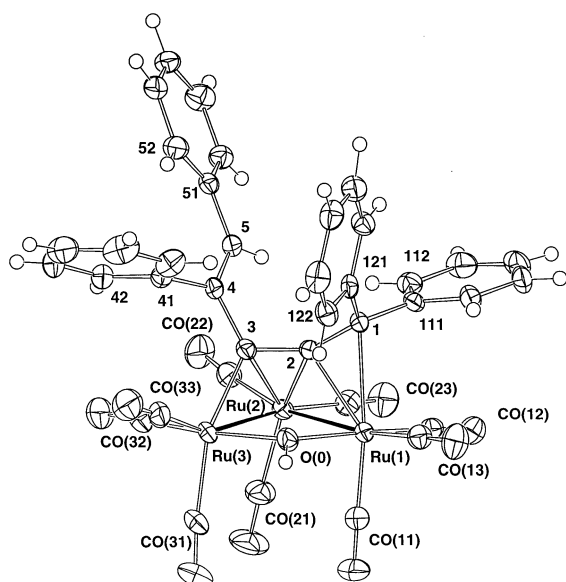


Fig. 6 Projection of a molecule of $\text{Ru}_3\{\mu_3\text{-Ph}_2\text{CCC(CPh=CHPh)}\}\text{(}\mu\text{-OH)(CO)}_9$ (7).

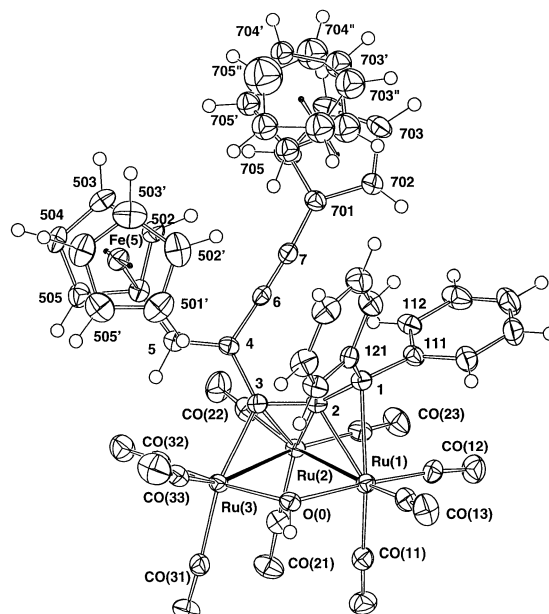


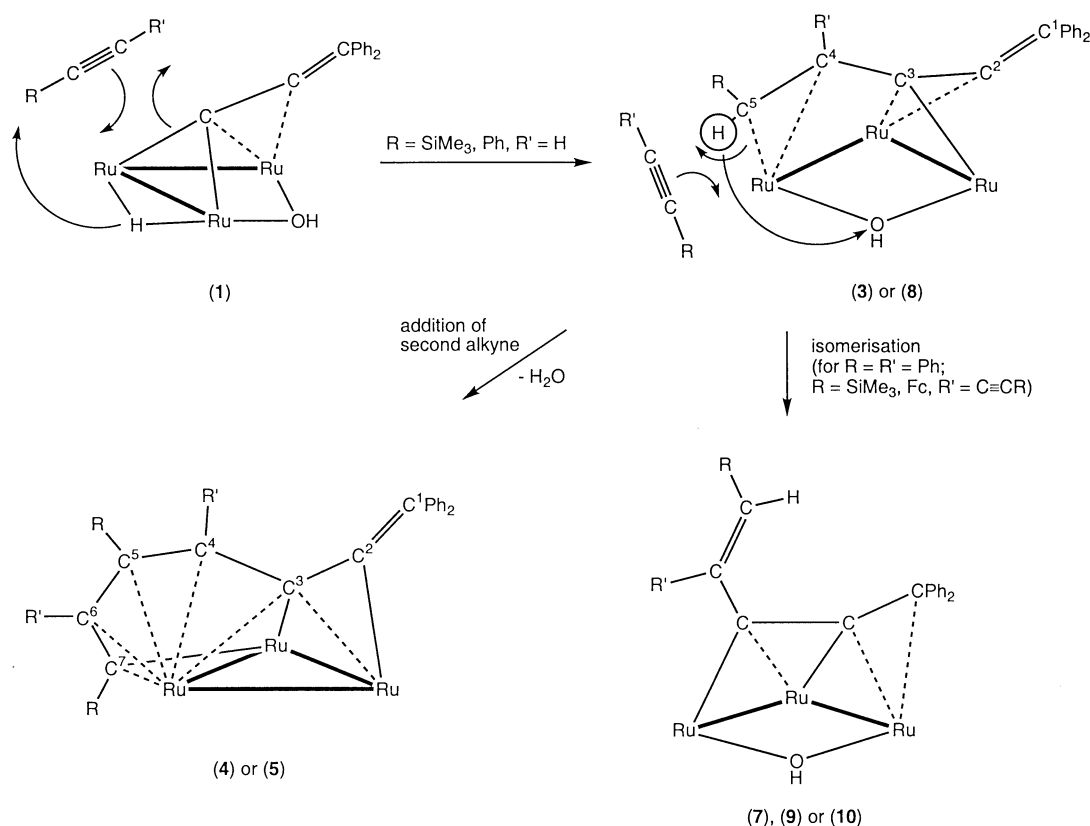
Fig. 8 Projection of a molecule of $\text{Ru}_3\{\mu_3\text{-Ph}_2\text{CCCC(C}\equiv\text{CFc)=CHFc}\}\text{(}\mu\text{-OH)(CO)}_9$ (10).

considered as a donor bond (in that direction), analogous to similar bonds in $\text{Ru}_2(\mu\text{-C}_4\text{R}_4)(\text{CO})_6$ complexes. A possible route to this arrangement is *via* insertion of the alkyne into an Ru–C bond, followed by migration of the cluster-bonded H atom to the organic ligand (Scheme 4).

The reaction between **1** and $\text{PhC}\equiv\text{CPh}$ affords the mono-addition product **7**, in which the alkyne appears as part of the *cis*-1,2-diphenylethenyl substituent borne by a μ_3 -diphenylallyl ligand. In this case, all three carbons of the CCCPh_2 skeleton have become linked to the Ru_3 cluster, with formation of a new C(3)–C(4) σ bond and concomitant migration of the cluster-bonded H atom to C(5). Complexes with a structure similar to **7** are formed from **1** and the 1,3-diyne $\text{RC}\equiv\text{CC}\equiv\text{CR}$ ($\text{R} = \text{SiMe}_3, \text{Fc}$), in which one of the $\text{C}\equiv\text{C}$ triple bonds has undergone the same insertion and addition of H. However, we noted that the first product formed in the reaction of $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$ has an isomeric structure, closely related to that of **3**. In this case, formal insertion into one of the Ru–C σ bonds of **1** has also occurred. Isomerisation to **9**, which occurs upon gentle heating, results in displacement of C(4)–

C(5) from the cluster and coordination of C(1), the organic ligand migrating along the Ru_3 array to allow coordination of C(1). We surmise that similar precursors may be formed and isomerise to **7** and **10**. Finally, we note that the Ru(2)–Ru(3) separations in **3** and **8** are unusually long, although there is no evidence for the presence of any bridging ligands, such as H, other than the organic ligand. In **9** and **10**, the organic ligand has a similar bonding mode to that found for several conventional allenyl complexes *via* attachment to the 1,2-diene portion [C(1)–C(2)–C(3)],¹⁵ whereas for those in **3** and **8**, the ligand is a linkage isomer in which the two η^2 interactions the 1,3-diene portion [C(2)–C(3)–C(4)–C(5)]. In both cases, however, the Ru–C σ bond involves C(3).

Where a second molecule of alkyne is added, initial coordination to the cluster, followed by insertion into the Ru–C(5) bond with C–C bond formation and concomitant elimination of water formed from the cluster OH group and (probably) the alkyne H atom, occurs. The loss of water during addition of the second molecule of alkyne is interesting. Hydrido-alkynyl complexes derived from substituted propargyl alcohols are



Scheme 4

known to dehydrate under forcing conditions, such as reactions with strong acids or adsorption onto silica gel.^{3,16} On the other hand, treatment of **2** on silica gel with water regenerates the hydrido-alkynyl $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}_2\text{CPh}_2(\text{OH}))(\text{CO})_9$.⁷ Possible mechanisms of these two, apparently independent, reaction pathways have been discussed.⁷

A final point of interest is the ^1H chemical shift of the cluster-bound OH groups, which is found between $\delta -5.25$ and -5.49 . This assignment of these peaks is supported by their disappearance upon addition of D_2O , together with the presence of $\nu(\text{OH})$ bands in the IR spectrum at *ca* 3600 cm^{-1} . The structural studies of **3** and **7–10** also confirm the presence of $\mu\text{-OH}$ ligands. Re-examination of the ^1H NMR spectrum of **1** showed a singlet at $\delta -5.86$, now assigned to the OH proton, together with one at $\delta -10.96$, arising from the cluster-bonded proton. Resonances of OH groups on clusters are rarely reported and, to our knowledge, have not been found before in this ^1H NMR spectral region.

Conclusions

The work described above has demonstrated the ready C–C bond formation between a cluster-bonded allenylidene ligand and alkynes or 1,3-diyne to give a variety of ligand structures which preserve at least one of the C=C double bonds of the allenylidene. Formal insertion into an Ru–C σ bond appears to be a common step in these reactions, although when relatively bulky substituents are present, this may be followed by isomerisation. Further experiments are required to define more precisely the course of these reactions and the factors which influence the nature of the products obtained from particular alkynes.

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 b.p. range $60\text{--}80\text{ }^\circ\text{C}$. Elemental analyses were performed by the Canadian Microanalytical Service, Delta, B.C., Canada. Preparative t.l.c. was carried out on glass plates ($20 \times 20\text{ cm}$) coated with silica gel (Merck 60 GF₂₅₄, 0.5 mm thickness).

Instrumentation

IR: Perkin Elmer 1720X FT IR. NMR: Bruker CXP300 or ACP300 (^1H at 300.13 , ^{13}C at 75.47 MHz) or Varian Gemini 200 (^1H at 199.8 , ^{13}C at 50.29 MHz) spectrometers. 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.¹⁷

Reagents

$\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C=C=CPh}_2)(\mu\text{-OH})(\text{CO})_9$ was prepared as previously described.⁴

Reactions of $\text{Ru}_3(\mu_3\text{-CCCPh}_2)(\mu\text{-OH})(\text{CO})_9$ (**1**)

(a) $\text{HC}\equiv\text{CSiMe}_3$. A reaction between $\text{HC}\equiv\text{CSiMe}_3$ (50 mg , 0.5 mmol) and $\text{Ru}_3(\mu_3\text{-CCCPh}_2)(\mu\text{-OH})(\text{CO})_9$ (120 mg , 0.16 mmol) in CH_2Cl_2 (5 ml) was carried out at r.t. for 1 h . Product isolation by t.l.c. (silica gel, acetone–hexane $1:10$) gave two fractions. Very dark red crystals (from $\text{CH}_2\text{Cl}_2\text{-MeOH}$) of $\text{Ru}_3\{\mu_3\text{-Me}_3\text{SiCCHC}(\text{SiMe}_3)\text{CHCC=CPh}_2\}(\text{CO})_8$ (**4**; head-to-tail isomer) (35 mg , 25%) were obtained from a dark purple band (R_f 0.68). Anal. found: C, 43.05 ; H, 3.39 ; $\text{C}_{33}\text{H}_{30}\text{O}_8\text{Ru}_3\text{Si}_2$ calcd.: C, 43.37 ; H, 3.29% ; M , 913 . IR (cyclohexane): $\nu(\text{CO})$ 2080s , 2050vs , $2039(\text{sh})$, 2020vs , 2010vs , 2003m , 1983w , 1953m cm^{-1} . ^1H NMR: δ 0.23 , 0.48 ($2 \times \text{s}$, $2 \times 9\text{H}$, $2 \times \text{SiMe}_3$), 6.88 (s, 1H , CH), 6.91 (s, 1H , CH), $7.12\text{--}7.56$ (m, 10H , Ph). An orange band (R_f 0.32) afforded $\text{Ru}_3(\mu_3\text{-Me}_3\text{SiCHCHCC=CPh}_2)\text{-}$

(μ -OH)(CO)₉ (**3**) (28 mg, 21%) as orange crystals (from CH₂Cl₂-MeOH). Anal. found: C, 40.26; H, 2.94; C₂₉H₂₂-O₁₀Ru₃Si calcd.: C, 40.42; H, 2.56%; *M*, 861. IR (cyclohexane): ν (OH) 3620; ν (CO) 2087m, 2067vs, 2040vs, 2019m, 2010s, 1995m, 1983m, 1952vw cm⁻¹. ¹H NMR: δ 0.31 (s, 9H, SiMe₃), 2.26 [d, 1H, *J*(HH) 1.62, CH], 3.25 [d, 1H, *J*(HH) 1.62 Hz, CH], 7.26–7.82 (m, 10H, Ph). ES mass spectrum (MeOH, *m/z*): 894, [M + MeOH]⁻; 865–754, [M + MeOH - *n*CO]⁻ (*n* = 1–4).

(b) With HC≡CPh. A mixture of HC≡CPh (29 mg, 0.28 mmol) and Ru₃(μ -H)(μ_3 -CCCPh₂)(μ -OH)(CO)₉ (110 mg, 0.14 mmol) in CH₂Cl₂ (7 ml) was stirred at r.t. for 1 h., after which time the colour had become dark red. Two isomeric products were isolated and purified by repeated preparative t.l.c. (silica gel, CH₂Cl₂-hexane 1:4). The first red band (*R_f* 0.52) afforded Ru₃(μ_3 -PhCCHCPhCHCC=CPh₂)(CO)₈ (**5b**; head-to-tail isomer) as a red solid (11.5 mg, 8.8%). IR (cyclohexane): ν (CO) 2083m, 2074w, 2056s, 2044m, 2023vs, 2014m, 2007m, 1996 (sh), 1985vw, 1960w cm⁻¹. ¹H NMR: δ 4.69 (s, 1H, CH), 5.02 (s, 1H, CH), 6.66–7.67 (m, 20H, Ph). The second purple band (*R_f* 0.49) gave Ru₃(μ_3 -PhCCHCPhCC=CPh₂)(CO)₈ (**5a**; head-to-head isomer) (8 mg, 6%) as dark red crystals (CHCl₃-MeOH). Anal. found: C, 48.52; H, 2.71; C₃₉H₂₂O₈Ru₃ calcd.: C, 50.81; H, 2.39%; *M*, 921. IR (cyclohexane): ν (CO) 2083m, 2074w, 2056s, 2044m, 2023vs, 2014m, 2007m, 1996 (sh), 1985vw, 1960w cm⁻¹. ¹H NMR: δ 6.37 [d, 1H, *J*(HH) 3.6, CH], 6.63 [d, 1H, *J*(HH) 3.6 Hz, CH], 6.95–7.55 (m, 20H, Ph). ES mass spectrum (MeOH containing NaOH, *m/z*): 954, [M + OMe]⁻; 923, M⁻; 895–811, [M - *n*CO]⁻ (*n* = 1–4). Both complexes are unstable in solution and readily decompose during work-up.

(c) With HC≡CFc. A similar reaction between HC≡CFc (54 mg, 0.26 mmol) and Ru₃(μ_3 -CCCPh₂)(μ -OH)(CO)₉ (100 mg, 0.13 mmol) in CH₂Cl₂ (5 ml) was carried out at r.t. for 1 h. Preparative t.l.c. (acetone-hexane 1:4) revealed a multitude of variously coloured products were present. Dark red crystals (from C₆H₆-pentane) of Ru₃{ μ_3 -(FcCCH)₂CC=CPh₂}(CO)₉ (**6**) (15.2 mg, 10%) were obtained as the only tractable material from a red band (*R_f* 0.47). Anal. found: C, 53.83; H, 4.41; C₄₈H₃₀Fe₂O₉Ru₃·1.5C₆H₆ calcd.: C, 53.35; H, 3.04%. IR (cyclohexane): ν (CO) 2097m, 2063m, 2053m, 2044m, 2023vs, 2010 (sh), 1992m, 1972w, 1958w cm⁻¹. ¹H NMR: δ 3.85 (s, 10H, Cp), 4.10, 4.25, 4.84 (3 × m, 8H, 2 × C₃H₄), 5.31 (s, 2H, 2 × CH), 6.96–7.49 (m, 10H, Ph).

(d) With PhC≡CPh. A mixture of Ru₃(μ_3 -CCCPh₂)(μ -OH)(CO)₉ (100 mg, 0.13 mmol) and PhC≡CPh (23 mg, 0.13 mmol) in CH₂Cl₂ (5 ml) was stirred at r.t. for 30 min. Separation by preparative t.l.c. (acetone-hexane 1–4) gave a major orange-red band (*R_f* 0.36) which contained orange crystalline Ru₃(μ_3 -Ph₂CCCCPh=CHPh)(μ -OH)(CO)₉ (**7**) (41.2 mg, 33%). Anal. found: C, 50.07; H, 2.98; C₃₈H₂₂O₁₀Ru₃ calcd.: C, 50.20; H, 2.55%. IR (cyclohexane): ν (OH) 3637; ν (CO) 2088m, 2067s, 2039vs, 2016s, 1995m, 1981w cm⁻¹. ¹H NMR: δ -5.31 (s, 1H, OH), 6.25 (s, 1H, CH), 6.75–7.56 (m, 20H, Ph). Several other compounds were present in small amounts, together with intractable decomposition products.

(e) With Me₃SiC≡CC=CSiMe₃. The reaction between Me₃SiC≡CC=CSiMe₃ (36 mg, 0.18 mmol) and Ru₃(μ_3 -CCCPh₂)(μ -OH)(CO)₉ (140 mg, 0.18 mmol) was carried out in CH₂Cl₂ (7 ml) at r.t. for 2 h. A single orange product (from CH₂Cl₂-pentane), identified as Ru₃{ μ_3 -Me₃SiCHC(C≡CSiMe₃)CC=CPh₂}(μ -OH)(CO)₉ (**8**), was purified by preparative t.l.c. (acetone-hexane 1:4), giving an orange band (*R_f* 0.80). Yield: 155 mg (88%). Anal. found: C, 42.70; H, 3.30; C₃₄H₃₀O₁₀Ru₃Si₂ calcd.: C, 42.63; H, 3.16%; *M*, 959. IR (cyclohexane): ν (OH) 3629; ν (CO) 2085m, 2067vs, 2040s, 2019 (sh), 2011m, 1995w (br), 1984w (br) cm⁻¹. ¹H NMR: δ -0.21, 0.48 (2 × s, 2 × 9H,

Table 2 Crystal data and refinement details

Compound	3	4	5a	6	7	8	9	10
Formula	C ₂₉ H ₂₂ O ₁₀ Ru ₃ Si·CH ₄ O	C ₃₃ H ₃₀ O ₈ Ru ₃ Si ₂	C ₃₉ H ₂₂ O ₈ Ru ₃	C ₄₈ H ₃₀ Fe ₂ O ₉ Ru ₃ ·C ₆ H ₆	C ₃₈ H ₂₂ O ₁₀ Ru ₃ ·2C ₆ H ₆	C ₃₄ H ₃₀ O ₁₀ Ru ₃ Si ₂	C ₃₄ H ₃₀ O ₁₀ Ru ₃ Si ₂ ·C ₆ H ₆	C ₃₈ H ₃₀ Fe ₂ O ₁₀ Ru ₃
MW	893.83	913.99	921.82	1243.78	1098.02	957.99	1036.10	1181.66
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> ₂ / <i>1</i> / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> ₂ / <i>1</i> / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> ₂ / <i>1</i> / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> ₂ / <i>1</i> / <i>c</i>
<i>a</i> /Å	13.398(4)	11.847(7)	17.990(4)	16.889(1)	10.840(1)	12.1663(6)	10.1882(8)	17.094(3)
<i>b</i> /Å	13.138(3)	19.100(5)	17.483(7)	18.235(1)	11.345(1)	18.6509(9)	13.178(1)	13.413(2)
<i>c</i> /Å	10.210(4)	17.467(7)	13.184(5)	15.578(1)	19.726(2)	16.5147(8)	16.074(2)	18.535(3)
α /°	80.98(2)	112.49(4)	107.88(3)	104.117(2)	82.429(2)	96.171(1)	85.469(3)	92.187(4)
β /°	76.48(2)	103.46(3)	103.46(3)	88.921(2)	88.921(2)	96.171(1)	89.050(3)	92.187(4)
γ /°	89.61(2)	108.70(2)	108.70(2)	68.909(2)	68.909(2)	96.171(1)	77.973(3)	92.187(4)
<i>V</i> /Å ³	1725	3477	3477	4652	2243	3726	2104	4247
<i>Z</i>	2	4	4	4	2	4	2	4
<i>D_c</i> /g cm ⁻³	1.721	1.662	1.759	1.775	1.626	1.708	1.635	1.848
μ /cm ⁻¹	13.9	13.4	13.4	16.2	10.6	13.2	11.7	17.7
Crystal size/mm	0.09 × 0.19 × 0.32	0.38 × 0.36 × 0.21	0.20 × 0.07 × 0.09	0.40 × 0.35 × 0.30	0.24 × 0.23 × 0.20	0.13 × 0.13 × 0.08	0.15 × 0.10 × 0.04	0.18 × 0.10 × 0.05
<i>T</i> ^{min,max} /°	0.79, 0.88	0.63, 0.74	0.85, 0.92	0.67, 0.83	0.66, 0.83	0.71, 0.86	0.86, 0.89	0.64, 0.79
2 θ _{max} /°	50	50	50	75	58	58	75	75
<i>N</i> _{tot}	—	—	—	94806	46051	78142	44024	88304
<i>N</i> (<i>R</i> _{int})	6063	6413	12220	24348 (0.037)	11802 (0.036)	9909 (0.11)	14196 (0.045)	15151 (0.091)
<i>N</i> _o (<i>n</i>)	4026 (3)	5104 (2)	5695 (3)	17035 (2)	9191 (2)	6826 (2)	9853 (2)	8668 (2)
<i>R</i>	0.057	0.039	0.046	0.034	0.033	0.033	0.039	0.042
<i>R_w</i>	0.068	0.041	0.042	0.041	0.038	0.029	0.039	0.036
$ \Delta\rho_{\text{max}} /e \text{ \AA}^{-3}$	1.41(5)	0.47(3)	1.6(3)	1.5(1)	1.58(6)	0.9(1)	2.0(1)	1.4(1)

2 × SiMe₃), 2.23 (s, 1H, CH), 7.21–7.75 (m, 10H, Ph). ES mass spectrum (MeOH, *m/z*): 988, [M + OMe – 2H]⁺.

On heating in refluxing CH₂Cl₂ for 30 min, **8** (22 mg) was completely converted to Ru₃{μ₃-Ph₂CCCC(C≡CSiMe₃)=CH(SiMe₃)}(μ-OH)(CO)₉ (**9**). This complex was obtained as yellow crystals (20 mg, 91%; C₆H₆-pentane) from a yellow band (*R_f* 0.56). Anal. found: C, 44.88; H, 3.54; C₃₄H₃₀O₁₀Ru₃Si₂·0.5C₆H₆ calcd.: C, 44.53; H, 3.31%; *M*, 959. IR (cyclohexane): ν(OH) 3633w; ν(CO) 2086m, 2066s, 2040vs, 2017s, 2014s, 1998m (br), 1984m, 1974 (sh), 1954vw cm⁻¹. ¹H NMR: δ –5.25 (1H, s, OH), 0.00, 0.17 (2 × s, 2 × 9H, 2 × SiMe₃), 6.38 (s, 1H, CH), 7.15–7.87 (m, 10H, Ph). ES mass spectrum (MeOH, *m/z*): 988, [M + OMe – 2H]⁺. This complex decomposes rapidly when dissolved in polar solvents.

(f) With FcC≡CC≡CFc. A solution containing FcC≡CC≡CFc (53 mg, 0.13 mmol) and Ru₃(μ₃-CCCPh₂)(μ-OH)(CO)₉ (100 mg, 0.13 mmol) in CH₂Cl₂ (7 ml) was stirred at r.t. for 2 h. Purification by preparative t.l.c. (acetone–hexane 1–4) separated an orange band (*R_f* 0.47) which afforded Ru₃{μ₃-Ph₂CCCC(C≡CFc)=CHFc}(μ-OH)(CO)₉ (**10**) (32.5 mg, 21%) as dark red crystals (hexane). Anal. found: C, 47.60; H, 2.58; C₄₈H₃₀Fe₂O₁₀Ru₃ calcd.: C, 48.80; H, 2.56%; *M*, 1183. IR (cyclohexane): ν(OH) 3632w; ν(CO) 2093vw, 2084w, 2070s, 2047vs, 2039 (sh), 2017m, 2007vs, 1992w, 1984w cm⁻¹. ¹H NMR: δ –5.49 (s, 1H, OH), 4.05, 4.40 (2 × s, 2 × 5H, 2 × Cp), 4.14–4.26, 4.49–4.77 (2 × m, 2 × 4H, 2 × C₅H₄), 6.18 (s, 1H, CH), 7.13–7.80 (m, 10H, Ph). This complex is unstable in solution and in contact with silica gel.

Structure determinations

For **3**, **4** and **5a**, room-temperature single counter diffractometer data sets (*T* ca. 295 K; 2θ scan mode, 2θ_{max} as specified; monochromatic Mo-Kα radiation, λ = 0.71073 Å) were measured to the specified level of redundancy. *N*_{total} reflections (where other than unique) were merged after Gaussian absorption correction, to *N* unique (*R*_{int} cited where appropriate), *N*_o with *I* > *nσ*(*I*) being used in the full matrix least squares refinement on |*F*|, minimising Σ*w*Δ² and refining anisotropic thermal parameters for the non-hydrogen atoms, (*x*, *y*, *z*, *U*_{iso})_H being constrained at estimates. For the remainder, full spheres of low-temperature CCD area-detector data were measured (*T* ca. 153 K; ω-scans; Bruker AXS instrument), to which 'empirical'/multiscan absorption corrections were applied, those with *F* > 4σ(*F*) being considered observed. Data, sometimes from rather small specimens, were generally of good quality albeit weak, with solvent molecules adversely affecting the adequacy of the refinement model on occasion. Conventional residuals *R*, *R*_w (statistical weights) are quoted at convergence. Neutral atom complex scattering factors were employed, computation using the XTAL 3.7 program system.¹⁸ Pertinent results are given in the Tables and Figures, the latter showing 20 (295) or 50% (153 K) 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.

Variata. 3. (*x*, *y*, *z*, *U*_{iso})_H for hydrogen atoms H(4,5) were not refinable and their postulation is a composite of difference map and chemical evidence, as also those of the OH groups on both the cluster and the solvent. The latter are hydrogen-bonded [O(0) ··· O(01), O(01) (2 – *x*, *y*, *z*) being 2.84(1), 2.74(1) Å. H(5) ··· O(0) is 2.5₅ Å].

4, 5a. As with **3**, H(4,6), H(*n*5, 6) were located from difference map/chemical considerations.

6. (*x*, *y*, *z*, *U*_{iso})_H were refined throughout, except for the benzene solvate.

7. All hydrogen atoms were located confidently from difference maps. H(122) ··· O(0) is 2.3₈ Å.

8, 9. All (*x*, *y*, *z*, *U*_{iso})_H were refined. In **8**, H(5) ··· O(0) is 2.39(3) Å; in **9**, H(122) ··· O(0) is 2.39(4) Å.

10. Cp ring 6' is rotationally disordered over two sets of sites, modelled with occupancies 0.5 after trial refinement, with isotropic thermal parameter forms. H(122) ··· O(0) is 2.3₂ Å.

CCDC reference numbers 175557–175564.

See <http://www.rsc.org/suppdata/dt/b1/b111088h/> for crystallographic data in CIF or other electronic format.

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