# Reactivity of multi-site bound allenylidene towards alkynes and silica gel†

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Heating the allenylidene species $[Ru_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}C=C=CPh_2)]$ in the presence of alkynes $RC_2R$ (R = Me or Ph) led to formation of the novel complexes $[Ru_3(CO)_9\{\mu_3\text{-}C(R)C(R)C_2CPh_2\}]$ (R = Me or Ph) and $[Ru_4(CO)_{12}\{\mu_4\text{-}C(Ph)C(Ph)CCCPh_2\}]$, shown by X-ray diffraction to contain $C_5$ ligands formed through carbon–carbon bond formation with the α-carbon of the allenylidene unit. Adsorption of $[Ru_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}C=C=CPh_2)]$ onto silica gel at room temperature leads to formation of the acetylide species $[Ru_3(CO)_9(\mu\text{-}H)\{\mu_3\text{-}C\equiv CC(Ph)_2OH\}]$, whereas reaction of $[Ru_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}C=C=C(Ph)Me\}]$ with silica gel affords $[Ru_3(CO)_9(\mu\text{-}H)\{\mu_3\text{-}C\equiv CC(Ph)=CH_2\}]$, containing an ene-yne ligand. Some insights into the mechanisms by which the transformations take place are given.

## Introduction

The recent interest in allenylidene complexes stems partly from the proposed involvement of these ligands in carbon chain growth processes at a metal surface.[1] Cluster complexes containing allenylidene ligands bound to more than two metal atoms offer the potential to model the surface-mediated reactivity of such organic fragments. However, examples of multi-site bound allenylidene complexes in the literature are rare[1–3] and accounts of their carbon–carbon bond forming reactions limited to the work of Bruce and co-workers on phenyl migration in the dppm-substituted complex $[Ru_3(CO)_7(\mu\text{-}CO)(\mu\text{-}dppm)(\mu_3\text{-}CCCPh_2)]$[4] and the reactivity of $[Ru_3(CO)_9(\mu\text{-}OH)(\mu\text{-}H)(\mu_3\text{-}CCCPh_2)]$ 1 towards terminal alkynes $HC\equiv CR$ (R = Ph or $SiMe_3$).[1] Interestingly, reaction of 1 with $HC\equiv C\text{-}SiMe_3$ was found to proceed via carbon–carbon bond formation between the alkyne and the α-carbon of the allenylidene ligand and hydride migration to afford the μ-hydroxide species $[Ru_3(CO)_9(\mu\text{-}OH)\{\mu_3\text{-}CH(SiMe_3)C(H)CC=CPh_2\}]$ 2 (see Scheme 1). Complex 2 may add a second molecule of alkyne, resulting in loss of water from the cluster and formation of $[Ru_3(CO)_8\{\mu_3\text{-}C(SiMe_3)C(H)C(SiMe_3)C(H)CC=CPh_2\}]$ 3a. Employing phenylacetylene in the reaction does not allow isolation of an intermediate species, instead the bis-alkyne derivative 3b is formed directly along with an isomer derived from tail to tail linkage of the incoming alkynes. It should be noted that each of the two steps in the above reaction involves either the μ-H or the μ-OH of the allenylidene cluster 1 in some way. The high yield synthesis of the μ₃-allenylidene complex $[Ru_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}CCCPh_2)]$ 4a, described previously,[3] presents an ideal opportunity to explore the reactivity of this ligand when co-ordinated to an unsubstituted ruthenium carbonyl centre and to make a comparison with the work of Bruce et al., described above. We report here on the reactivity of 4a towards the internal alkynes but-2-yne and diphenylacetylene, which leads to the formation of metallacyclic complexes containing $C_5$ ligands bridging three ruthenium atoms in an unprecedented manner. In addition, the reaction with diphenylacetylene affords small amounts of a novel 'flat-butterfly'
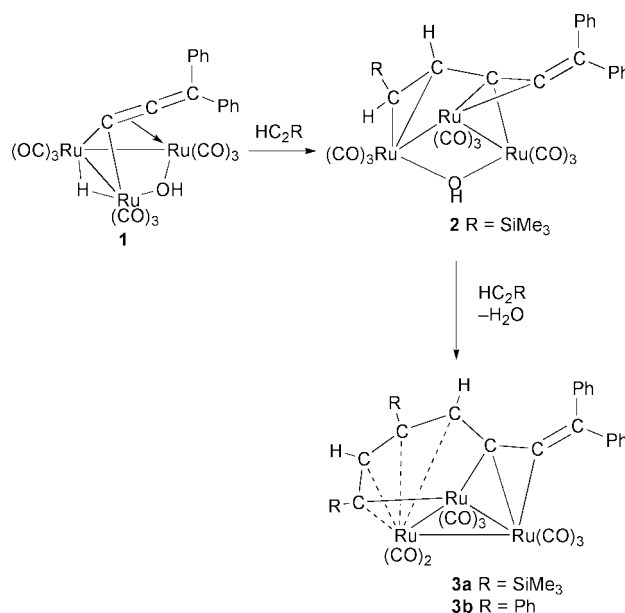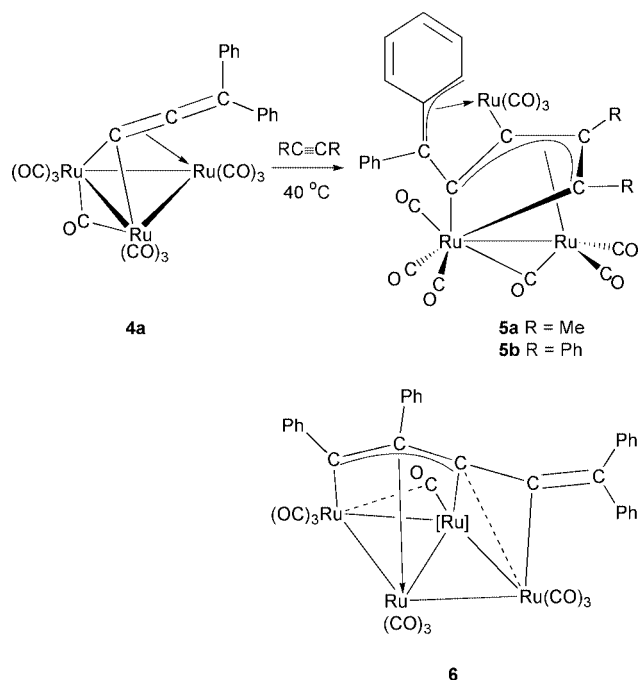


**Scheme 1**

tetraruthenium complex containing a $C_5$ chain. We also include an account of the 'surface-mediated' transformations of the complexes $[Ru_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}CCC(Ph)R\}]$ (R = Ph 4a or R = Me 4b) that occur on silica gel and vary according to the nature of the R substituent.

## Results and discussion

Heating complex 4a at 40 °C in the presence of an excess of alkyne afforded $[Ru_3(CO)_9\{\mu_3\text{-}C(Me)C(Me)C_2CPh_2\}]$ 5a (30%), in the case of but-2-yne, and $[Ru_3(CO)_9\{\mu_3\text{-}C(Ph)C(Ph)C_2CPh_2\}]$ 5b (20%) and $[Ru_4(CO)_{12}\{\mu_4\text{-}C(Ph)C(Ph)CCCPh_2\}]$ 6 (5%) in the case of diphenylacetylene (see Scheme 2). The molecular structures of the new complexes were all determined by X-ray diffraction studies and are discussed later. The spectroscopic data are consistent with the solid state structures. Thus, the IR spectra of complexes 5 show the presence of eight terminal carbonyl bands and a stretch at about 1950 cm$^{-1}$ indicative of an asymmetrically bridging carbonyl unit.[5] The ¹H

**Scheme 2**



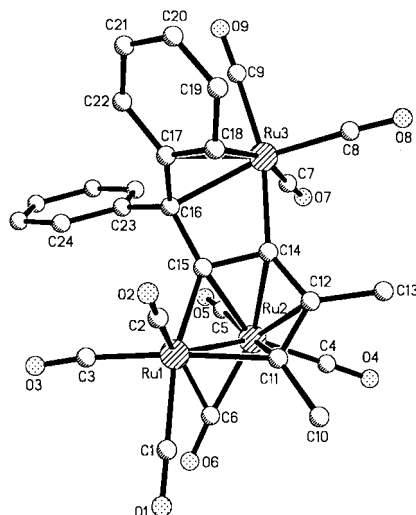**Fig. 1** Molecular geometry of complex **5a**; all hydrogen atoms have been omitted for clarity (as in all the present structures).

NMR spectra each show the presence of phenyl protons in the region $\delta$ 7.76–6.74 and a doublet of doublets ($\delta$ 6.06 **5a**; 6.18 **5b**) for the proton attached to the metal-bound *ortho*-carbon of the phenyl group. This slight up-field shift from the normal aromatic phenyl region compares well with those seen for the corresponding protons of di-[6] and tri-ruthenium[7] complexes containing similar metal–phenyl $\pi$ interactions. The IR spectrum of complex **6** also indicates the presence of a semi-bridging carbonyl ligand (1916 cm$^{-1}$), as well as containing bands for terminal carbonyls, whilst the $^1$H NMR spectrum showed only a multiplet due to phenyl protons centered at $\delta$ 7.45. Owing to the low yield of **6** no satisfactory $^{13}$C NMR data could be obtained but the FAB mass spectrum and elemental analysis were consistent with the solid state structure.

The mechanism by which complexes **5** are formed is unclear but formally involves the following processes: loss of one molecule of CO; cleavage of two Ru–Ru bonds; insertion of an alkyne unit into one of the metal–allenylidene $\sigma$ bonds of **4a**; co-ordination of $C_\gamma$ and a phenyl group of the original allenylidene ligand to a ruthenium atom in $\eta^3$ fashion. Di- and tri-nuclear complexes containing metallacyclopentadienyl ligands are common products from reaction of metal carbonyl complexes of the iron triad with alkynes[8] and this ligand type has also been observed in complexes containing transition metals other than those of Group 8.[9] However, the complexes **5** show some noteworthy features. First, they represent extremely rare examples of metallacyclopentadienyl ligands in which one of the ring carbons has been metallated. Secondly, we could find only three examples in the literature of metallacyclopentadienyl ligands containing ligating substituents at the 1 or 2 positions, the complexes [Ru$_3$Pt(CO)$_7$(dppe){$\mu_4$-C(Bu$^t$)-C(H)C(CHCBu$^t$)C(CBu$^t$)}{$\mu$-C(H)C(H)(Bu$^t$)}],[10] [Ru$_3$(CO)$_8$-{RCC(Ph)C(Ph)CR}] (R = C(H)C(H)Ph)[11] and [Os$_3$(CO)$_9$-{C(SiMe$_3$)C(Me)C(H)CR}] (R = aryl or ferrocenyl).[12] The first two examples each contain an exocyclic vinyl group co-ordinated to a metal atom. The last example represents a series of complexes containing *ortho*-metallated ferrocenyl or aryl substituents on one of the $C_1$ carbons. Thirdly, this is the first time such a metallacyclopentadienyl unit has been obtained directly from allenylidene. Interestingly, the complex [Fe$_2$(CO)$_6$-{$\mu$-Ph(H)CCCHC(OMe)O}], containing a penta-atomic metallacycle, was reported in 1997 from reaction of the allenylidene species [Fe$_3$(CO)$_9$($\mu$-CO){$\mu_3$-CCC(Ph)H}] with meth-

anol in the presence of silica gel.[13] Further, *closo*-pentagonal bipyramidal clusters [Fe$_3$(CO)$_6$($\mu$-CO)$_2$(RC$_2$R$^1$)$_2$] and 'ferrole' complexes [Fe$_2$(CO)$_6$(RC$_2$R$^1$)$_2$] are common by-products in the thermolysis of propargyl alcohols and [Fe$_3$(CO)$_{12}$], leading to formation of allenylidene complexes [Fe$_3$(CO)$_9$($\mu$-CO){$\mu_3$-CCC-(R)R$^1$}].[8,13–15] It was assumed that these metallacyclopentadienyl by-products are the result of alkynol dimerisation and cluster fragmentation. However, in the light of the above results it is tempting to suggest that at least some of these products are a direct result of the desired allenylidene complex reacting with the excess of alkynol under the reaction conditions.

It was mentioned in the introduction that one of the reasons for the interest in allenylidene ligands is their proposed involvement in carbon chain-growth processes. Thus, it is noteworthy that metallacyclopentadienyl ligands have been found as intermediates in a range of such processes, including Ziegler–Natta catalysis,[16] olefin polymerisation,[17] alkyne oligomerisation,[18] hydro-oligomerisation of alkynes,[19] alkyne cycloaddition[20] and the synthesis of tropones.[21]

Of the products obtained from our allenylidene–alkyne linking reactions, only the tetraruthenium complex **6** bears any resemblance to those products obtained by Bruce and co-workers in that it contains a $C_5$ chain similar to that seen in **2** (formed from alkyne linkage with the $\alpha$-carbon of the allenylidene ligand). However, the formation of the chain in complex **2** involved hydrogen migration from the cluster to one of the alkyne carbons, a process which may not occur for the unsubstituted cluster **4a**. Instead, formation of **6** has involved cluster expansion so that the pentacarbon backbone of the ligand now bridges four ruthenium atoms in a hitherto unseen manner. Formally, complex **6** may be derived from **5b** *via* addition of one unit of Ru(CO)$_3$ and so we decided to investigate whether **6** was a simple decomposition product of **5b**. However, thermolysis of **5b** under a range of reaction conditions led to isolation of starting material or decomposition products other than **6** which were not identified.

### Molecular structures of complexes 5

The molecular structures of complexes **5a** and **5b** are shown in Figs. 1 and 2 respectively. Selected bond lengths and angles for **5a** are given in Table 1 whereas those of **5b** are available as supplementary data (ESI†). The two sets of structural parameters were extremely similar and all of the bond lengths and angles used in the discussion below are those of **5a**, unless otherwise stated.

The complexes **5** each contain three ruthenium atoms of which only Ru(1) and Ru(2) are within bonding distance
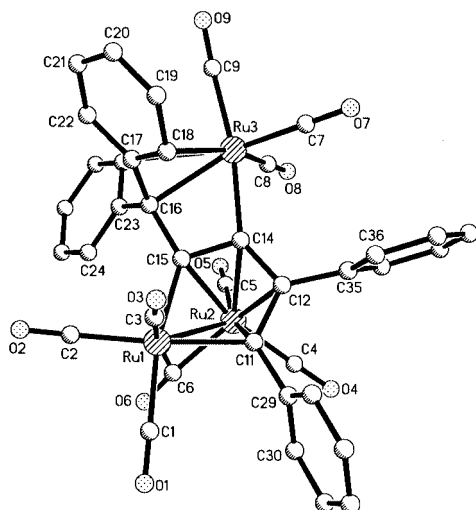
**Fig. 2** Molecular geometry of complex **5b**.



**Fig. 3** Molecular geometry of complex **6**.

**Table 1** Selected bond lengths [Å] and angles [°] for complex **5a**

| | | | |
|---|---|---|---|
| Ru(1)–C(15) | 2.095(3) | Ru(3)–C(18) | 2.390(3) |
| Ru(1)–C(11) | 2.113(3) | C(6)–O(6) | 1.147(4) |
| Ru(1)–Ru(2) | 2.7140(6) | C(10)–C(11) | 1.509(4) |
| Ru(1)···C(6) | 2.813(4) | C(11)–C(12) | 1.414(5) |
| Ru(2)–C(6) | 1.904(4) | C(12)–C(14) | 1.430(4) |
| Ru(2)–C(15) | 2.233(3) | C(12)–C(13) | 1.522(4) |
| Ru(2)–C(11) | 2.273(3) | C(14)–C(15) | 1.415(4) |
| Ru(2)–C(14) | 2.292(3) | C(15)–C(16) | 1.526(4) |
| Ru(2)–C(12) | 2.303(3) | C(16)–C(17) | 1.445(4) |
| Ru(3)–C(14) | 2.095(3) | C(16)–C(23) | 1.515(4) |
| Ru(3)–C(16) | 2.260(3) | C(17)–C(18) | 1.439(4) |
| Ru(3)–C(17) | 2.341(3) | | |
| | | | |
| C(15)–Ru(1)–C(11) | 76.43(13) | C(10)–C(11)–Ru(2) | 128.2(2) |
| C(15)–Ru(1)–Ru(2) | 53.48(9) | Ru(1)–C(11)–Ru(2) | 76.37(10) |
| C(11)–Ru(1)–Ru(2) | 54.48(9) | C(11)–C(12)–C(14) | 113.8(3) |
| Ru(2)–Ru(1)–C(6) | 40.24(8) | C(11)–C(12)–C(13) | 125.1(3) |
| C(15)–Ru(2)–C(11) | 70.55(11) | C(14)–C(12)–C(13) | 121.1(3) |
| C(15)–Ru(2)–C(14) | 36.42(11) | C(11)–C(12)–Ru(2) | 70.87(19) |
| C(11)–Ru(2)–C(14) | 62.90(12) | C(14)–C(12)–Ru(2) | 71.48(18) |
| C(15)–Ru(2)–C(12) | 63.94(11) | C(13)–C(12)–Ru(2) | 128.0(2) |
| C(11)–Ru(2)–C(12) | 35.99(12) | C(15)–C(14)–C(12) | 115.2(3) |
| C(14)–Ru(2)–C(12) | 36.27(11) | C(15)–C(14)–Ru(3) | 100.6(2) |
| C(6)–Ru(2)–Ru(1) | 72.67(11) | C(12)–C(14)–Ru(3) | 143.5(2) |
| C(15)–Ru(2)–Ru(1) | 48.92(8) | C(15)–C(14)–Ru(2) | 69.52(18) |
| C(11)–Ru(2)–Ru(1) | 49.15(8) | C(12)–C(14)–Ru(2) | 72.25(19) |
| C(14)–Ru(2)–Ru(1) | 73.30(8) | Ru(3)–C(14)–Ru(2) | 130.43(15) |
| C(12)–Ru(2)–Ru(1) | 73.75(8) | C(14)–C(15)–C(16) | 104.5(3) |
| C(14)–Ru(3)–C(16) | 64.45(12) | C(14)–C(15)–Ru(1) | 116.6(2) |
| O(6)–C(6)–Ru(2) | 170.3(3) | C(16)–C(15)–Ru(1) | 135.6(2) |
| O(6)–C(6)–Ru(1) | 122.6(3) | C(14)–C(15)–Ru(2) | 74.06(19) |
| Ru(2)–C(6)–Ru(1) | 67.09(11) | C(16)–C(15)–Ru(2) | 132.2(2) |
| C(12)–C(11)–C(10) | 118.1(3) | Ru(1)–C(15)–Ru(2) | 77.60(11) |
| C(12)–C(11)–Ru(1) | 117.0(2) | C(17)–C(16)–C(15) | 114.9(3) |
| C(10)–C(11)–Ru(1) | 124.3(3) | C(15)–C(16)–Ru(3) | 90.44(19) |
| C(12)–C(11)–Ru(2) | 73.14(19) | | |

[Ru(1)–Ru(2) 2.7140(6) Å], with Ru(3) having non-bonding distances of 4.761 and 3.984 Å to Ru(1) and Ru(2), respectively. Rutheniums (1) and (3) each are bonded to three terminal carbonyl ligands and Ru(2) to two. In addition, the Ru(1)–Ru(2) bond is asymmetrically bridged by a carbonyl unit [Ru(1)–C(6) 2.813(4), Ru(2)–C(6) 1.904(4) Å; Ru(2)–C(6)–O(6) 170.3°], with the six terminal carbonyls around the metal–metal bond held in a non-sawhorse arrangement. The asymmetric nature of the bridging carbonyl unit is more pronounced in complex **5b**, having an Ru(2)–C(6)–O(6) angle of 161.5° and Ru(1)–C(6) and Ru(2)–C(6) bond lengths of 2.603(4) and 1.921(5) Å respectively. The C₅ fragments in each complex are clearly formed through linkage of C(12) of an alkyne molecule (but-2-yne **5a**; diphenylacetylene **5b**) with the α-carbon [C(14)] of the allenylidene unit in **4a**, and bridge all three metal atoms.
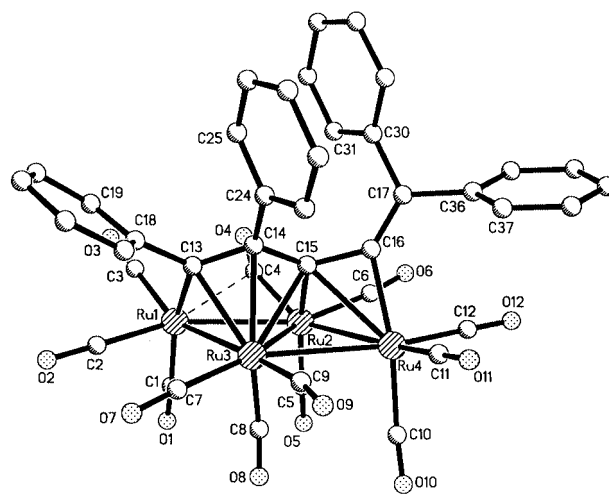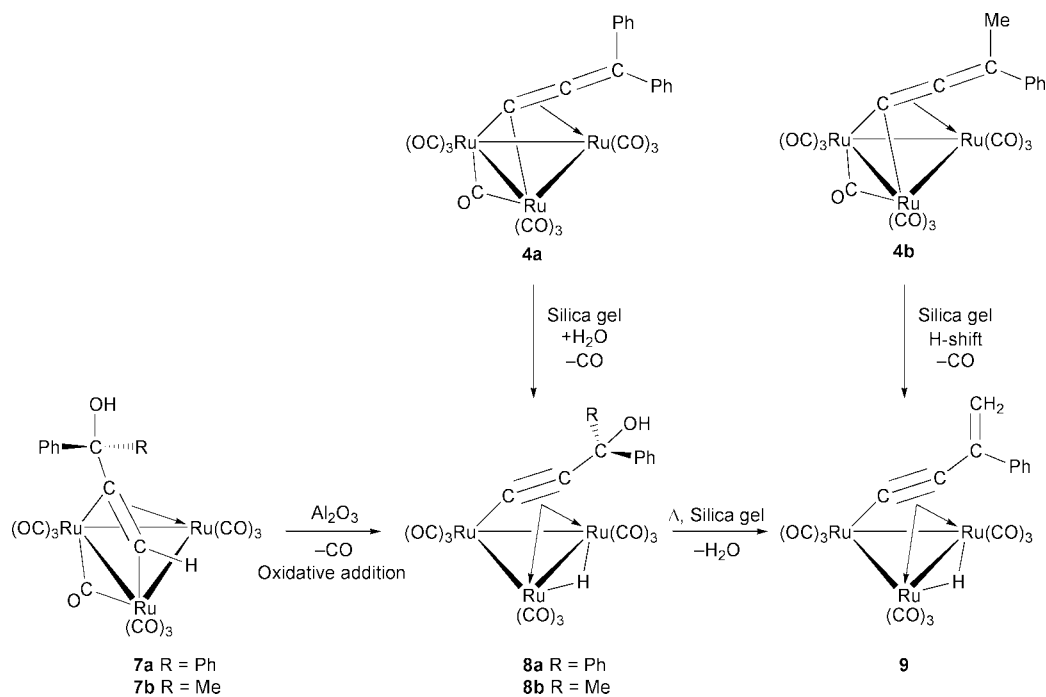
Thus, carbons C(11)–C(15) form a metallacyclic unit through two σ-type bonds to Ru(1) [Ru(1)–C(11) 2.113(3) and Ru(1)–C(15) 2.095(3) Å], all four carbons of which interact with Ru(2) in an η⁴ manner [with all Ru–C bonds in the range 2.203(3)–2.333(3) Å]. The C(11)–C(12), C(12)–C(14) and C(14)–C(15) bond lengths of 1.414(5), 1.430(4) and 1.415(4) Å respectively suggest some delocalisation of the π-electron density over these three bonds. The γ-carbon [C(16)] of the original allenylidene unit, and the *ortho* [C(17)] and *meta* [C(18)] carbons of one of its phenyl substituents, form an allylic type fragment [C(16)–C(17) 1.445(4), C(17)–C(18) 1.439(4) Å] which interacts in an η³ fashion with Ru(3) [Ru(3)–C(16) 2.260(3), Ru(3)–C(17) 2.314(3) and Ru(3)–C(18) 2.390(3) Å]. Related interactions have previously been observed in some dimetallic aryl-substituted μ-carbene complexes.[5,22] The involvement of the phenyl ring in bonding to Ru(3) results in some delocalisation of the π-electron density in the remaining intra-ring C–C bonds such that two [C(19)–C(20) 1.354(5), C(21)–C(22) 1.351(5) Å] are shorter than the other three [all greater than 1.415(5) Å]. A strong σ bond from C(14) to Ru(3) [2.095(3) Å] completes the bonding. The above, along with the spectroscopic data, suggests complexes **5** are best represented as shown in Scheme 2, *i.e.* as μ₃-butadienyl species with a diphenylcarbene substituent which binds in η³-allyl fashion to one of the ruthenium atoms. Considering **5a** and **5b** as simple 'ruthenole'-type complexes in which the metallacyclopentadienyl ring has been metallated allows us to assign them as having *nido*-pentagonal bipyramidal geometries.

**Molecular structure of complex 6**

The structure of complex **6** is shown in Fig. 3 and selected bond lengths and angles in Table 2. The tetraruthenium complex has 62 valence electrons and adopts the planar rhomboid ('flat butterfly') arrangement observed previously for such cluster compounds as [Ru₄(CO)₈(μ-PPh₂)₂(C₄Buᵗ₂)].[23] Thus, the fold angle between the wings is 4.1° and the four rutheniums form a plane (mean deviation 0.045 Å). Some distortion of the metal framework is suggested by the long peripheral Ru(3)–Ru(4) bond distance of 3.0306(11) Å. The longest of the remaining peripheral Ru–Ru bonds, the Ru(1)–Ru(2) vertex, is asymmetrically bridged by the C(4)O(4) carbonyl unit. The main point of interest in complex **6** stems from the presence of an unusual bridging moiety that binds to the metal centre in a manner not previously reported. Thus, carbons C(13)–(17) form the C₅ backbone of a μ₄-organic unit derived from carbon–carbon bond formation between C(14) of a molecule of diphenylacetylene and the α-carbon [C(15)] of the allenylidene unit in complex **4a**. The ligand formally donates a total of six electrons to the metal centre *via* three σ bonds [Ru(1)–C(13)

Ph
|
C
‖
C
‖
(OC)₃Ru———Ru(CO)₃
O‖C
Ru
(CO)₃

Me
|
C—Ph
‖
C
‖
(OC)₃Ru———Ru(CO)₃
O‖C
Ru
(CO)₃

**4a**    **4b**

Silica gel
+H₂O
−CO

Silica gel
H-shift
−CO

OH
|
Ph—C⋯R
|
C
‖
(OC)₃Ru———Ru(CO)₃
C—H
O‖C
Ru
(CO)₃

Al₂O₃
−CO
Oxidative addition

R   OH
\ /
C—Ph
‖
C
(OC)₃Ru———Ru(CO)₃
H
Ru
(CO)₃

Λ, Silica gel
−H₂O

CH₂
‖
C—Ph
‖
C
(OC)₃Ru———Ru(CO)₃
H
Ru
(CO)₃

**7a** R = Ph        **8a** R = Ph        **9**
**7b** R = Me        **8b** R = Me

**Scheme 3**

**Table 2**  Selected bond lengths [Å] and angles [°] for complex **6**

| | | | |
|---|---|---|---|
| Ru(1)–C(13) | 2.122(3) | Ru(3)–C(15) | 2.414(3) |
| Ru(1)⋯C(4) | 2.585(3) | Ru(3)–Ru(4) | 3.0306(11) |
| Ru(1)–Ru(3) | 2.7883(9) | Ru(4)–C(16) | 2.113(3) |
| Ru(1)–Ru(2) | 2.8178(10) | Ru(4)–C(15) | 2.516(3) |
| Ru(2)–C(4) | 1.899(4) | C(4)–O(4) | 1.150(4) |
| Ru(2)–C(15) | 2.091(3) | C(13)–C(14) | 1.416(4) |
| Ru(2)–Ru(4) | 2.7733(9) | C(14)–C(15) | 1.443(4) |
| Ru(2)–Ru(3) | 2.7970(8) | C(15)–C(16) | 1.435(4) |
| Ru(3)–C(13) | 2.323(3) | C(16)–C(17) | 1.341(4) |
| Ru(3)–C(14) | 2.324(3) | | |
| | | | |
| C(13)–Ru(1)–Ru(3) | 54.43(8) | C(16)–Ru(4)–Ru(2) | 72.92(9) |
| C(13)–Ru(1)–Ru(2) | 84.50(8) | C(15)–Ru(4)–Ru(2) | 46.25(7) |
| C(4)–Ru(1)–Ru(2) | 40.87(7) | C(16)–Ru(4)–Ru(3) | 81.55(9) |
| Ru(3)–Ru(1)–Ru(2) | 59.86(2) | C(15)–Ru(4)–Ru(3) | 50.57(7) |
| C(15)–Ru(2)–Ru(4) | 60.39(9) | Ru(2)–Ru(4)–Ru(3) | 57.42(2) |
| C(15)–Ru(2)–Ru(3) | 57.03(8) | O(4)–C(4)–Ru(2) | 160.2(3) |
| Ru(4)–Ru(2)–Ru(3) | 65.92(3) | O(4)–C(4)–Ru(1) | 123.4(3) |
| C(4)–Ru(2)–Ru(1) | 62.96(10) | Ru(2)–C(4)–Ru(1) | 76.17(11) |
| C(15)–Ru(2)–Ru(1) | 86.14(9) | C(14)–C(13)–Ru(1) | 125.2(2) |
| Ru(4)–Ru(2)–Ru(1) | 125.33(2) | C(14)–C(13)–Ru(3) | 72.30(17) |
| Ru(3)–Ru(2)–Ru(1) | 59.55(2) | Ru(1)–C(13)–Ru(3) | 77.57(10) |
| C(13)–Ru(3)–C(14) | 35.48(10) | C(13)–C(14)–C(15) | 119.9(3) |
| C(13)–Ru(3)–C(15) | 62.96(10) | C(13)–C(14)–Ru(3) | 72.21(17) |
| C(14)–Ru(3)–C(15) | 35.41(10) | C(15)–C(14)–Ru(3) | 75.72(17) |
| C(13)–Ru(3)–Ru(1) | 48.00(8) | C(16)–C(15)–C(14) | 123.2(3) |
| C(14)–Ru(3)–Ru(1) | 75.69(8) | C(16)–C(15)–Ru(2) | 112.4(2) |
| C(15)–Ru(3)–Ru(1) | 81.09(7) | C(14)–C(15)–Ru(2) | 124.1(2) |
| C(13)–Ru(3)–Ru(2) | 81.50(7) | C(16)–C(15)–Ru(3) | 124.1(2) |
| C(14)–Ru(3)–Ru(2) | 74.91(7) | C(14)–C(15)–Ru(3) | 68.87(16) |
| C(15)–Ru(3)–Ru(2) | 46.59(7) | C(16)–C(15)–Ru(4) | 73.37(9) |
| Ru(1)–Ru(3)–Ru(2) | 60.60(2) | C(14)–C(15)–Ru(4) | 133.14(19) |
| C(13)–Ru(3)–Ru(4) | 116.57(7) | Ru(2)–C(15)–Ru(4) | 73.37(9) |
| C(14)–Ru(3)–Ru(4) | 85.10(8) | Ru(3)–C(15)–Ru(4) | 75.82(9) |
| C(15)–Ru(3)–Ru(4) | 53.61(8) | C(17)–C(16)–C(15) | 133.5(3) |
| Ru(1)–Ru(3)–Ru(4) | 117.14(2) | C(17)–C(16)–Ru(4) | 137.5(2) |
| Ru(2)–Ru(3)–Ru(4) | 56.663(19) | C(15)–C(16)–Ru(4) | 88.2(2) |
| C(16)–Ru(4)–C(15) | 34.74(10) | | |

2.122(3), Ru(2)–C(15) 2.091(3) and Ru(4)–C(16) 2.113(3) Å]
and four π-interactions, of which the Ru(3)–C(15) and Ru(3)–
C(14) distances [2.414(3) and 2.324(3) Å, respectively] are
significantly longer than those of Ru(3)–C(13) and Ru(3)–C(14)
[2.323(3) and 2.324(3) Å], possibly reflecting the multi co-
ordinated nature of C(15). The bonds between C(13)–C(16)

span the narrow range 1.416(4)–1.443(4) Å suggesting delocal-
isation of the electron density across this four-carbon chain,
whereas the C(16)–C(17) distance of 1.341(4) Å is characteristic
of an unco-ordinated double bond.

**Transformations of [Ru₃(CO)₉(μ-CO){μ₃-CCC(Ph)R}] (R = Ph 4a or Me 4b) on silica gel**

There are several reports on the effect of supports, such as silica
gel and alumina, in promoting hydration and dehydration
reactions.[7,24] We have previously shown that the splitting and
addition of water[25] or methanol[13] to ene-yne or allenylidene
tri-iron derivatives occurs very easily on TLC silica. More
recently, our investigations into the behaviour of triruthenium
carbonyl complexes containing alkynol units (and ligands
derived therefrom) have led to some interesting results in this
area of 'surface organometallic chemistry'. Thus, the parallel
bound hydroxyalkyne complexes [Ru₃(CO)₉(μ-CO){μ₃-C(H)=
CC(Ph)(R)OH}] **7** are found to undergo decarbonylation and
oxidative addition of the alkyne on alumina to yield the corre-
sponding acetylide species [Ru₃(CO)₉(μ-H){μ₃-C≡CC(Ph)(R)-
OH}] **8** (see Scheme 3).[3] Further, adsorption of **8b** (R = Me)
onto silica gel and heating at 100 °C was found to facilitate
dehydration of the acetylide unit, yielding small amounts
of the ene-yne-containing species [Ru₃(CO)₉(μ-H){μ₃-
C≡CC(Ph)=CH₂}] **9**.[27] We have now found that similar
processes may occur for the allenylidene complexes [Ru₃(CO)₉-
(μ-CO){μ₃-C=C=C(Ph)R}] **4**. Thus, complex **4a** (R = Ph) was
adsorbed onto silica gel and left at room temperature for 24 h,
after which time chromatography afforded the acetylide species
[Ru₃(CO)₉(μ-H){μ₃-C≡CC(Ph)₂OH}] **8a** in 20% yield. Employ-
ing **4b** (R = Me) in the same reaction yielded instead
[Ru₃(CO)₉(μ-H){μ₃-C≡CC(Ph)=CH₂}] **9** (30%), which contains
an ene-yne ligand. The complexes **8a** and **9** were readily char-
acterised by comparison of their spectroscopic data with those
in the literature.[26,27] It is clear from the above results that the
nature of the alkyne substituents plays a role in determining
the manner in which complexes **4** are transformed on silica gel.
For complex **4a** (R = Ph) the overall process involves loss of a
carbonyl unit and addition of water (split into its component
parts). However, **4b** (R = Me) has formally undergone decarb-
onylation and hydrogen migration from the alkyl substituent to
the cluster edge. Although we have no mechanistic details for

the processes our previous results in this area allow us to rule out some of the more likely pathways. It has previously been shown that protonation of the acetylide complex [Ru$_3$(CO)$_9$(μ-H){μ$_3$-C≡CC(Me)(Ph)OH}] **8b** affords the ene-yne species **9**[26,27] and so one might suggest that initially the complexes **4** undergo identical transformations on silica gel to afford the corresponding species [Ru$_3$(CO)$_9$(μ-H){μ$_3$-C≡CC(Ph)(R)OH}] **8**, with the methyl-substituted complex **8b** allowing a further process to occur, yielding the observed ene-yne product **9**. However, as mentioned earlier, transformation of **8b** to **9** on silica gel has been shown to require high temperatures and affords only trace amounts of product. Similarly, the initial conversion of complexes **4** into the corresponding alkynol species [Ru$_3$(CO)$_9$(μ-CO){μ$_3$-C(H)=CC(Ph)(R)OH}] **7** may be ruled out on the grounds that complexes **7** are stable on silica gel and rearrange only on alumina. Further, if this were the case one would expect employment of shorter reaction times to yield small amounts of **7**, which is not the case. We suggest, therefore, that the two silica gel-mediated transformations occur *via* independent pathways.

## Experimental

Reactions and general manipulations were performed under a nitrogen atmosphere using deoxygenated solvents, dried by distillation over an appropriate drying agent. Column chromatography was performed on silica gel. 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, FAB mass spectra using a Fisons Autospec instrument, proton and carbon-13 NMR spectra 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 alkynes but-2-yne (Aldrich) and diphenlyacetylene (Lancaster) were used as supplied. Silica gel 60 (Fluka) of Brockmann Activity 2–3 and particle size 0.2–0.5 mm (35–70 mesh ASTM) was used as supplied in the surface-mediated reactions. The complexes [Ru$_3$(CO)$_9$(μ-CO){μ$_3$-C=C=CPh(R)}] (R = Ph **4a** or Me **4b**) were prepared by the literature methods.[3]

### Reaction of [Ru$_3$(CO)$_9$(μ-CO)(μ$_3$-C=C=CPh$_2$)] 4a with but-2-yne

A dichloromethane solution (20 cm$^3$) of complex **4a** (175 mg, 0.23 mmol) and MeC≡CMe (110 μl, 1.40 mmol) was heated at reflux for 5 h. The solvent was removed, under reduced pressure, and the product chromatographed. A yellow band, eluted with CH$_2$Cl$_2$–hexane (1:5), yielded [Ru$_3$(CO)$_9${μ$_3$-C(Me)C(Me)C$_2$CPh$_2$}] **5a** (54 mg, 30%) as yellow crystals after recrystallisation from heptane at −20 °C [Found: C, 42.36; H, 2.12%; *M* (mass spectrometry) 800. C$_{28}$H$_{16}$O$_9$Ru$_3$ requires C, 42.06; H, 2.02%; *M* 800]. IR: $v_{CO}$ (heptane) 2081s, 2066vs, 2041vs, 2020m, 2008m, 1998 (sh)m, 1983s, 1968m and 1950w cm$^{-1}$. $^1$H NMR (CD$_2$Cl$_2$): δ 7.76–6.74 (9H, m, Ph), 6.06 (1H, dd, *J* = 2 and 5 Hz), 2.38 (3H, s, Me) and 2.29 (3H, s, Me). $^{13}$C NMR (CD$_2$Cl$_2$): δ 200.0, 199.5, 197.9, 197.6, 197.3, 196.5, 188.7 (CO), 172.2 (C15), 171.1 (C11), 141.8 (C14), 137.0, 139.0, 132.8, 128.8, 127.8 (all Ph), 126.0 (C16), 124.7 (C12), 91.2 (C17), 76.0 (C18), 30.7 (μ-C*Me*) and 16.9 (C*Me*). Assignments were aided by a DEPT 135° experiment.

### Reaction of [Ru$_3$(CO)$_9$(μ-CO)(μ$_3$-C=C=CPh$_2$)] 4a with diphenylacetylene

A dichloromethane solution (35 cm$^3$) of complex **4a** (200 mg, 0.26 mmol) and PhC≡CPh (138 mg, 0.78 mmol) was heated at reflux for 3 h. Removal of solvent and chromatography, eluting

with CH$_2$Cl$_2$–hexane (1:9), afforded both a yellow and a dark purple band. Recrystallisation of the yellow band from a CH$_2$Cl$_2$ solution layered with hexane afforded [Ru$_3$(CO)$_9${μ$_3$-C(Ph)C(Ph)C$_2$CPh$_2$}] **5b** (48 mg, 20%) as a crystalline solid. Recrystallisation of the dark purple band from a CH$_2$Cl$_2$ solution layered with hexane afforded [Ru$_4$(CO)$_{12}$(μ$_4$-C(Ph)C(Ph)CCCPh$_2$)] **6** (14 mg, 5%) as a crystalline solid.

**Complex 5b.** IR ($v_{CO}$) in heptane: 2084s, 2071vs, 2044vs, 2025m, 2009m, 1995 (sh)m, 1985s, 1970m and 1951w cm$^{-1}$. $^1$H NMR (CD$_2$Cl$_2$): δ 7.74–6.81 (19H, m, Ph) and 6.18 (1H, dd, *J* = 2 and 5 Hz). $^{13}$C NMR (CD$_2$Cl$_2$): δ 201.3, 199.3, 197.6, 195.7, 193.8, 193.5, 189.0 (CO), 171.2 (C15), 169.1 (C11), 142.2 (C14), 141.7, 139.5, 133.1, 132.0, 129.4, 128.7, 128.2, 127.9, 127.8, 127.6, 126.1, 123.8, 121.3 (all Ph), 136.7 (C16), 125.4 (C12), 89.4 (C17) and 74.8 (C18). Assignments were aided by a DEPT 135° experiment. FAB MS: *m/z* 924 (M$^+$) and 868–672 (M − *n*CO)$^+$ (*n* = 2–9). Found: C, 49.36; H, 2.16. Calc. C, 49.41; H, 2.18%.

**Complex 6.** IR ($v_{CO}$) in heptane: 2096s, 2074vs, 2046vs, 2038s, 2028s, 1986m, and 1916w cm$^{-1}$. $^1$H NMR (CD$_2$Cl$_2$): δ 7.83–6.92 (m, Ph). FAB MS: *m/z* 1108 (M$^+$) and 1080–772 (M − *n*CO)$^+$ (*n* = 1–12). Found: C, 44.46; H, 1.85. Calc: C, 44.41; H, 1.82%.

### Silica gel-mediated transformations of [Ru$_3$(CO)$_9$(μ-CO){μ$_3$-C=C=C(Ph)R}] (R = Ph 4a or Me 4b)

In each of the reactions described below the complexes were adsorbed onto silica gel by mixing a dichloromethane solution of the complex with silica gel in a flask and allowing the solvent to evaporate.

Complex **4a** (55 mg, 0.07 mmol) was adsorbed and left at room temperature for 24 h. Chromatography of the reaction mixture, eluting with CH$_2$Cl$_2$–hexane (1:9), afforded the yellow complex [Ru$_3$(CO)$_9$(μ-H){μ$_3$-C≡CC(Ph)$_2$OH}] **8a** (11 mg) in a yield of 20%. IR ($v_{CO}$) in heptane: 2101w, 2075s, 2055s, 2025vs and 1991m cm$^{-1}$. $^1$H NMR (CDCl$_3$): δ 7.77–7.24 (m, Ph), 2.64 (s, 1H) and −21.11 (s, 1H).

Complex **4b** (50 mg, 0.07 mmol) was adsorbed and left at room temperature for 24 h. Chromatography of the reaction mixture, eluting with CH$_2$Cl$_2$–hexane (1:8), afforded the yellow complex [Ru$_3$(CO)$_9$(μ-H){μ$_3$-C≡CC(Ph)=CH$_2$}] **9** (14 mg) in a yield of 30%. IR ($v_{CO}$) in heptane: 2099w, 2074s, 2055s, 2047m, 2026s and 1992m. $^1$H NMR (CD$_2$Cl$_2$): δ 7.64–7.27 (m, Ph), 5.72 (d, 1H), 5.61 (d, 1H) and −20.83 (s, 1H).

**Table 3** Crystallographic data for complexes **5a**, **5b** and **6**

|  | 5a | 5b | 6 |
|---|---|---|---|
| Formula | C$_{28}$H$_{16}$O$_9$Ru$_3$ | C$_{38}$H$_{20}$O$_9$Ru$_3$ | C$_{41}$H$_{20}$O$_{12}$Ru$_4$ |
| *M*/g mol$^{-1}$ | 799.6 | 923.8 | 1108.9 |
| Crystal system | Triclinic | Monoclinic | Triclinic |
| Space group | P$\bar{1}$ | P2$_1$/n | P$\bar{1}$ |
| *a*/Å | 9.244(1) | 13.279(2) | 9.232(3) |
| *b*/Å | 10.611(1) | 17.374(2) | 14.127(5) |
| *c*/Å | 14.171(2) | 15.161(2) | 15.478(3) |
| *a*/° | 82.23(1) |  | 83.66(2) |
| *β*/° | 84.14(1) | 102.73(1) | 82.26(2) |
| *γ*/° | 78.16(1) |  | 74.02(2) |
| *U*/Å$^3$ | 1344.0(3) | 3411.7(8) | 1917.1(9) |
| *Z* | 2 | 4 | 2 |
| *μ*/mm$^{-1}$ | 1.72 | 1.37 | 1.61 |
| Total data | 10016 | 35148 | 19421 |
| Unique data | 4668 | 7834 | 8649 |
| *R*$_{int}$ (%) | 3.0 | 3.7 | 3.6 |
| Observed data, No | 3783 | 6324 | 6102 |
| *R*1 (observed data) (%) | 2.3 | 2.2 | 2.6 |
| *wR*2 (all data) (%) | 4.8 | 5.2 | 5.5 |

**Crystal structure determinations of complexes 5a, 5b and 6**

Single crystals of complexes **5a**, **5b** and **6** were grown by diffusion of a hexane layer into dichloromethane solutions. Data were collected at −100 °C on a Bruker SMART diffractometer using graphite-monochromated Mo-Kα radiation. Other important experimental details are collected in Table 3.

CCDC reference number 186/2248.

See http://www.rsc.org/suppdata/dt/b0/b006780f/ for crystallographic files in .cif format.

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