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Acid promoted formation of tri- and penta-ruthenium allenylidene complexes

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A series of μ_3-(||) hydroxyalkyne derived species [$Ru_3(CO)_9(\mu$-CO){μ_3-C(H)=CC(R)OH(R^1)}] has been prepared. Unexpectedly, the complexes (where neither R nor R^1 = H) react with alumina to form the corresponding alkynyl species [$Ru_3(CO)_9(\mu$-H){μ_3-C_2C(R)OH(R^1)}], a transformation which may also be effected by thermolysis. More importantly, acid induced dehydration of the propargyl alcohol species [$Ru_3(CO)_9(\mu$-CO){μ_3-C(H)=CC(R)OH(R^1)}] (R = R^1 = Ph; R = Ph, R^1 = Me) leads to formation of the corresponding allenylidene complexes [$Ru_3(CO)_9(\mu$-CO)-{μ_3-C=C=C(Ph)R}] (R = Ph or Me), [$Ru_5(CO)_{15}(\mu_4$-C=C=CPh_2)] and [$Ru_5(CO)_{15}${μ_5-C=C=C(Ph)Me}]; the penta-ruthenium complexes have been shown by X-ray diffraction studies to contain unprecedented multi-site bound allenylidene ligands and different metal atom arrangements.

Introduction

The synthesis, reactivity and catalytic applications of cluster compounds containing unsaturated C_1 and C_2 hydrocarbyl ligands have played a major role in the development of organometallic chemistry.[1] More recently, complexes containing allenylidene have attracted attention and there are now numerous examples in the literature of mono- and di-nuclear transition metal complexes containing this ligand.[2] However, cluster bound allenylidenes remain relatively rare, trinuclear complexes of the iron triad in which the allenylidene bridges all three metal atoms in a 2σ, π fashion accounting for almost all of the reported examples.[2] To our knowledge the complex [$Ru_7(CO)_{19}${μ_4-CC(H)C(O)Me}{μ_5-CCC(H)Me}], formed as one of several products from the thermolysis of [$Ru_3(CO)_{12}$] with HC_2C(H)(Me)OH, represents the only example of an allenylidene moiety interacting with more than three metal atoms.[3] The formation of trinuclear complexes of the Group 8 metals containing allenylidene fragments has proven relatively straightforward for iron only. Several synthetic routes to complexes of the type [$Fe_3(CO)_9(\mu$-CO){μ_3-C=C=C(R)(R^1)}] **1** are known[4] including simple thermolysis of [$Fe_3(CO)_{12}$] in the presence of propargyl alcohols, which leads to formation of the desired allenylidene complex *via* spontaneous loss of water from the alkynol (see Scheme 1).[1] However, this process is not general for all propargyl alcohols[5] and the desired allenylidene containing species is often isolated in low yield as one of several products.[6]

In the case of ruthenium and osmium, heating of the appropriate carbonyl complex [$M_3(CO)_{12}$] and propargyl alcohols does not lead to dehydration but instead to oxidative addition and formation of the corresponding alkynyl complexes [$M_3(CO)_9(\mu$-H){μ_3-C_2C(R)OH(R^1)}] **2**.[7] Dehydration of these species may be effected by addition of acid. Thus, reaction of the complexes **2** (R or R^1 = alkyl) with acid results in loss of OH and one of the protons of the alkyl group and formation of the corresponding ene-yne species (*e.g.* **3**).[7b,c] This mode of dehydration may be prevented when both of the alkynol substituents are aryl groups, protonation instead leading to allenylidene complexes containing a variety of bridging ligands depending on the reaction conditions (*e.g.* complexes **4**,[7c,8,9] **5**[9] and **6**[9]). However, the ruthenium and osmium homologues of the unsubstituted triiron allenylidene complexes **1** have proven elusive. In this regard it is interesting that although protonation of **2** (M = Ru; R = R^1 = Ph) in the presence of bis(diphenylphosphino)methane (dppm) affords the dppm substituted species **5**, carrying out the reaction under an atmosphere of CO does not afford the corresponding allenylidene complex [$Ru_3(CO)_9(\mu$-CO){μ_3-C=C=C$(Ph)_2$}].[9]

We have synthesized a range of μ_3-(||) hydroxyalkyne derived complexes [$Ru_3(CO)_9(\mu$-CO){μ_3-C(H)=CC(R)OH(R^1)}] **7** (Scheme 2), and studied their reactivity towards acid. We report here that for R = Ph or Me, R^1 = Ph this leads to products containing allenylidene co-ordinated to three, four and five metal atoms. The structures of μ_3-, μ_4- and μ_5-allenylidene complexes have been determined crystallographically, with the μ_4 and μ_5 species showing hitherto unseen bonding modes for this ligand. In addition, the complexes **7** react with alumina to yield the corresponding alkynyl species [$Ru_3(CO)_9(\mu$-H)-{μ_3-C_2C(R)OH(R^1)}] **8** *via* loss of CO and oxidative addition of the alkyne to the metal centre. The same transformation may be effected by thermolysis[9] but the alumina mediated reactions show enhanced selectivity towards the alkynol substituents.

Results and discussion

Synthesis of the hydroxyalkyne complexes 7

The lightly ligated complex [$Ru_3(CO)_{10}(NCMe)_2$] has been shown to react with a range of alkynes (RC_2CR^1) under mild conditions, affording the corresponding μ_3-(||) alkyne species [$Ru_3(CO)_9(\mu$-CO)(μ_3-CR=CR^1)].[10,11] In keeping with these results, we have found that reaction of this complex with a variety of alkynols at room temperature leads to formation of the corresponding hydroxyalkyne derived species [$Ru_3(CO)_9$-(μ-CO){μ_3-C(H)=CC(R)OH(R^1)}] **7** in yields of 55–70%, based on moles of [$Ru_3(CO)_{12}$] used (see Scheme 2). While this work was in progress, Bruce *et al.* independently reported[9] the synthesis of complexes **7a** (R = R^1 = Ph), **7c** (R = R^1 = Me) and **7d** (R = R^1 = H) *via* the same route, making characterisation of the alkynol complexes straightforward. The relevant data for the

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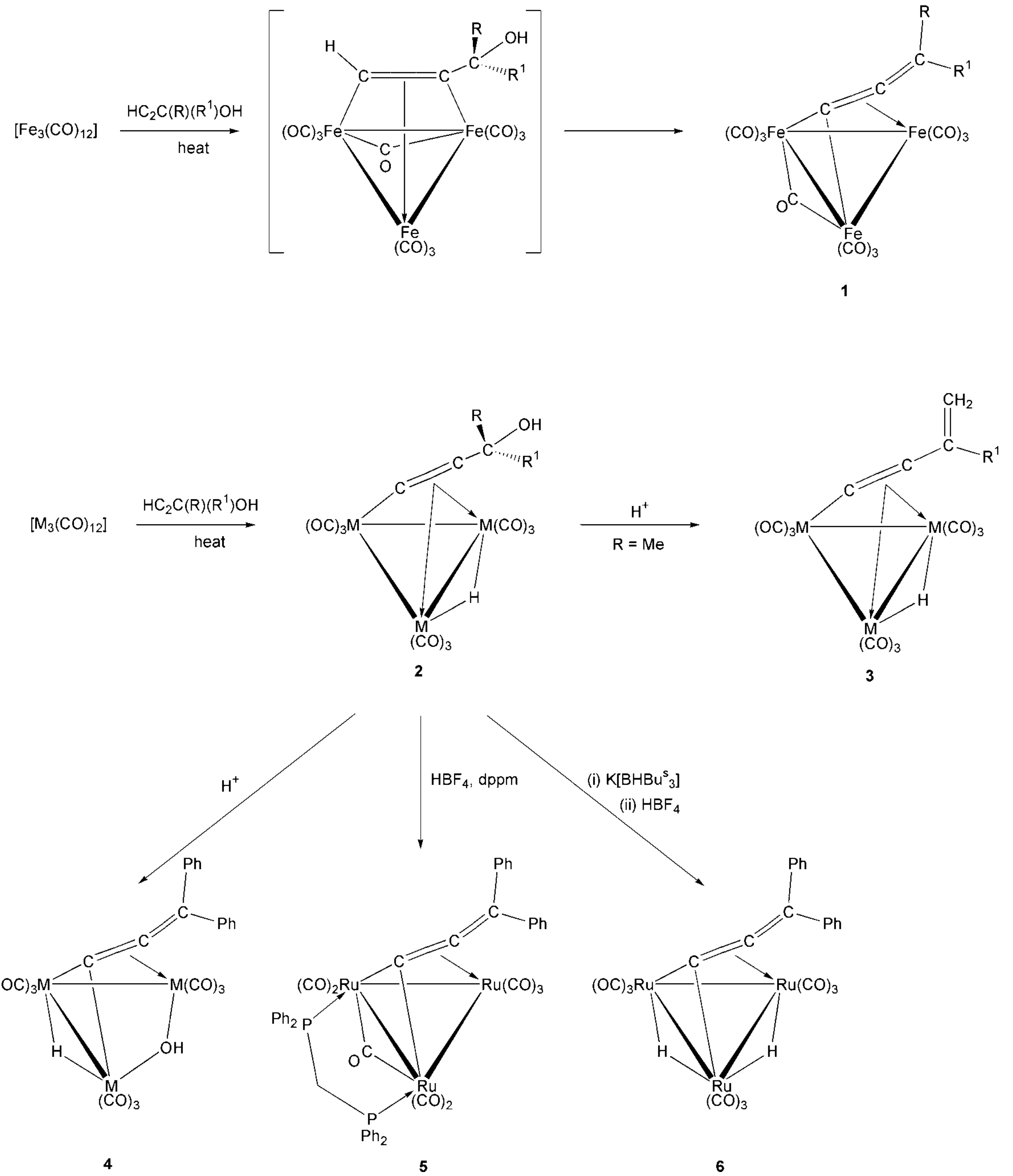


Scheme 1 M = Ru or Os.

new complexes **7b** (R = Ph, R^1 = Me) and **7e** (R = Ph, R^1 = H) are collected in Tables 1 and 2.

Decarbonylation of the hydroxyalkyne complexes 7

It has been shown that heating at reflux a solution of $[Ru_3(CO)_{12}]$ and propargyl alcohols in hydrocarbon solvents leads to formation, in moderate yields, of the corresponding alkynyl complexes $[Ru_3(CO)_9(\mu\text{-H})\{\mu_3\text{-}C_2C(R)OH(R^1)\}]$ **8**[7] only when neither of the substituents R or R^1 is a proton. Formation of alkynyl species *via* thermal decarbonylation of the corresponding μ_3-(||) alkynol complex has been demonstrated before for osmium, giving $[Os_3(CO)_9(\mu\text{-H})\{\mu_3\text{-}C_2C(H)_2OH\}]$.[12] Recently, Bruce *et al.* also showed that, upon thermolysis, the hydroxyalkyne species **7a**, **7c** and **7d** afford the corresponding alkynyl complexes **8** in high yield.[9] We have found a similar result from heating **7b** in hexane.

Unexpectedly, chromatography of the parallel bound species **7a**–**7c** on alumina leads to isolation of the corresponding alkynyl complexes **8a**–**8c** in yields of 30–60% and only small amounts of the desired alkynol complexes. Surface mediated reactions of cluster compounds containing propargyl alcohol units are not uncommon and there is an ever increasing number of examples involving inorganic oxides commonly used in chromatography (*e.g.* alumina and silica gel).[13] In the course of our studies we have identified several types of surface-mediated processes occurring for alkynol containing clusters, including dehydration[7c,14] and CO activation.[15] However, the above observed decarbonylation in association with oxidative addition represents a new type of inorganic oxide mediated reaction. It is interesting that, unlike the thermolytic reactions of complexes **7**, this ‘surface-mediated’ reactivity appears to depend on the nature of the R substituents on the alkynol. Thus, chromatography of **7d** or **7e** on alumina leads to some decomposition but does not afford any of the corresponding alkynyl species.

Protonation of the hydroxyalkyne complexes 7

Addition of $HBF_4{\cdot}OEt_2$ to complexes **7a**–**7e** results in formation of unidentified cationic species in varying yields. The cationic species are unstable as solids and in solution and have

Table 1 Analytical and physical data for new complexes

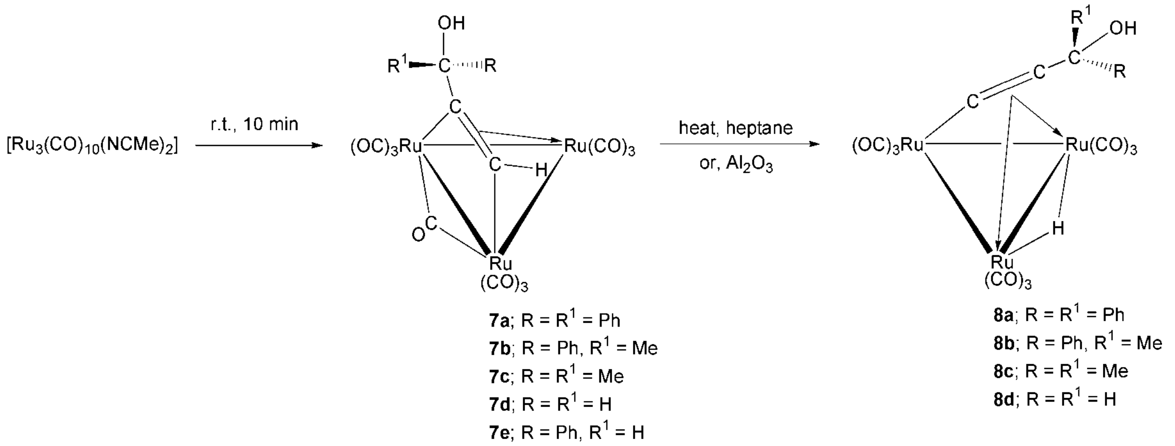
Complex	Colour	$M^{a,b}$	Analysis (%)[a,c] C	H
7b $[Ru_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}C(H){=}CC(Ph)OH(Me)\}]$	Orange	730(730)	33.14(32.93)	1.33(1.38)
7e $[Ru_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}C(H){=}CC(Ph)OH(H)\}]$	Orange	716(716)	[d]	[d]
11a $[Ru_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}C{=}C{=}C(Ph)_2\}]$	Purple	774(774)	38.97(38.80)[e]	1.33(1.30)
11b $[Ru_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}C{=}C{=}C(Ph)(Me)\}]$	Purple	745(745)	33.63(33.76)[e]	1.12(1.13)
12 $[Ru_5(CO)_{15}\{\mu_4\text{-}CC{=}C(Ph)_2\}]$	Green	1115(1115)	32.43(32.16)[e]	0.88(0.90)
13 $[Ru_5(CO)_{15}\{\mu_5\text{-}CC{=}C(Ph)Me\}]$	Dark red	1056(1056)	28.84(28.54)[e]	0.79(0.76)

[a] Calculated values in parentheses. [b] By mass spectrometry with fast atom bombardment ionisation. [c] Recrystallised from hexane unless otherwise stated. [d] Product isolated as an oil. [e] Recrystallised from heptane.

Table 2 IR and NMR data for new complexes

Complex	$\tilde{\nu}_{CO}{}^{a}$/cm^{-1}	^{1}H NMR (δ)[b]	^{13}C-{^{1}H} NMR (δ)[b]
7b	2098w, 2063vs, 2053vs, 2031s, 2009m, 1884w	8.38 (s, 1H), 7.40–7.15 (m, 5H), 2.22 (s, 1H), 1.40 (s, 3H)	197.6 (CO), 147.5 (μ-C), 140.9 (μ-CH), 128.6–124.8 (Ph), 83.0 (C–OH), 32.8 (Me)
7e	2098w, 2061vs, 2055vs, 2028s, 2012m, 1878w	8.30 (s, 1H), 7.40–7.10 (m, 5H), 2.20 (s, 1H, OH), 0.91 (s, 1H, CH)	198.0–196.0 (CO), 158.2 (μ-C), 130.0–128.0 (Ph), 127.8 (μ-CH), 53.4 (C–OH)
11a	2097m, 2068vs, 2051vs, 2034s, 2022s, 1996m, 1916m	7.36 (m)	211.7 (μ-CO), 195.0 (br, CO), 168.2 (C_α), 129.6 (C_β), 128.9–127.3 (2 × Ph), 115.2 (C_γ).
11b	2097m, 2068vs, 2051vs, 2034s, 2022s, 1995m, 1915m	7.36 (m, 5H), 2.36 (s, 3H)	213.9 (μ-CO), 195.1 (br, CO), 167.2 (C_α), 139.2 (C_β), 128.9–126.8 (Ph), 108.0 (C_γ), 22.9 (Me)
12	2181m, 2158vs, 2098vs, 2071vs, 2044m, 2007m	7.36 (m, 10H)	
13	2094m, 2063vs, 2031vs, 2019s, 2006s, 1999m, 1988m, 1954m	7.36 (m, 5H), 2.36 (s, 3H)	

[a] Heptane solution. [b] CD_2Cl_2 solution unless otherwise stated.

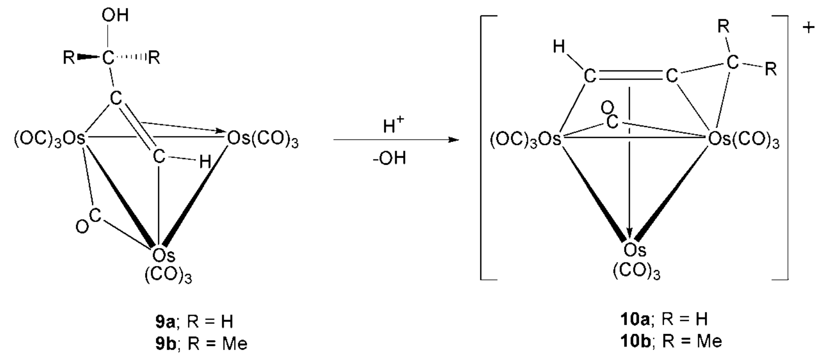


Scheme 2

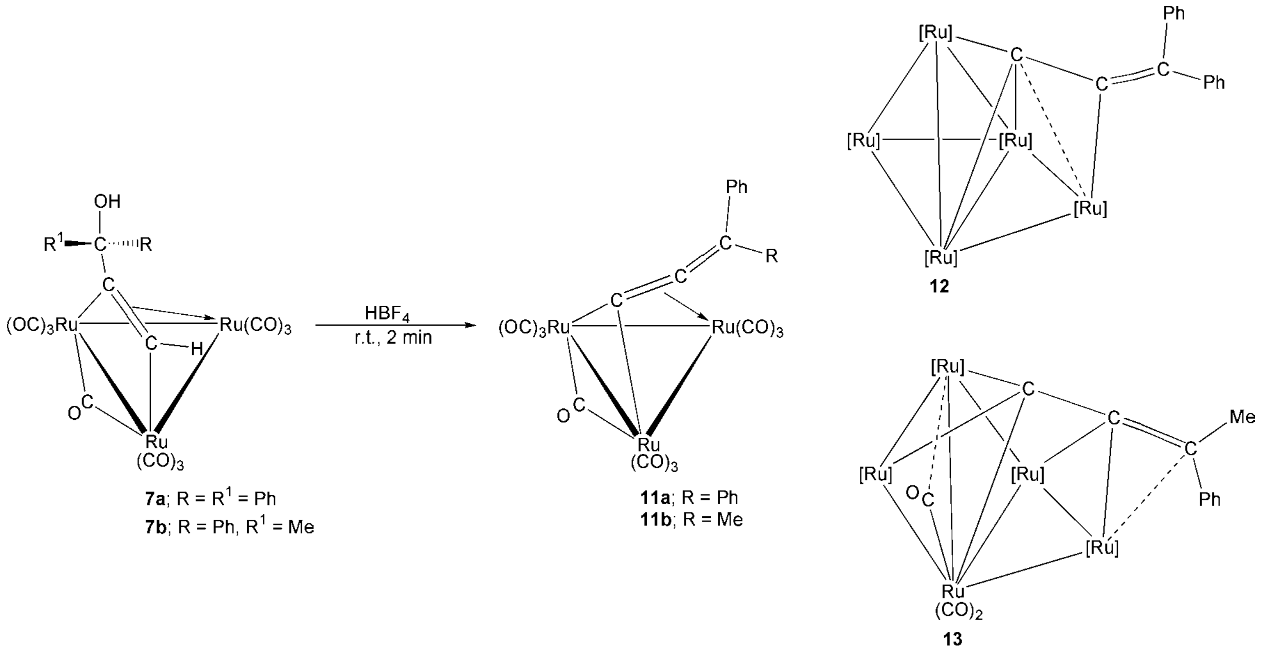
not yet been characterised. Previous protonation studies on the analogous triosmium clusters $[Os_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}HC{=}CC(R)_2OH\}]$ **9** also afforded unstable cationic complexes, which low temperature NMR studies suggested were the propargyl species $[Os_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}HC{\equiv}CC(R)_2\}]^+$ **10** (see Scheme 3).[12,16] Thus far, similar NMR studies on the cationic ruthenium compounds have not given any conclusive data (perhaps due to the instability of ruthenium compounds compared to osmium) and these investigations are ongoing.

Surprisingly, for the complexes $[Ru_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}C(H){=}CC(R)OH(R^1)\}]$ ($R = R^1 = Ph$ **7a**; $R = Ph$, $R^1 = Me$ **7b**) addition of acid leads to only small amounts of the cationic species, the major products being the neutral allenylidene complexes $[Ru_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}C{=}C{=}C(Ph)R\}]$ [R = Ph, 70% **11a**; Me, 59% **11b**], $[Ru_5(CO)_{15}(\mu_4\text{-}CC{=}CPh_2)]$ **12** (5%) and $[Ru_5(CO)_{15}\text{-}\{\mu_5\text{-}CC{=}C(Ph)Me\}]$ **13** (5%) (see Scheme 4). The IR spectra of the purple complexes **11** each contained six terminal carbonyl bands and one due to a bridging carbonyl (1916 **11a**; 1915 cm^{-1} **11b**). In the ^{13}C NMR spectra, resonances for the C_3 units were observed at δ 168.2 (C_α), 129.6 (C_β) and 115.2 (C_γ) for **11a** and 167.2 (C_α), 139.2 (C_β) and 108.0 (C_γ) for **11b**. These data agree well with those reported for the analogous complex $[Ru_3(CO)_7\text{-}(\mu\text{-}CO)(\mu\text{-}dppm)(\mu_3\text{-}C{=}C{=}CPh_2)]$ **5** of δ 169.2, 143.8.6 and 113.3, respectively.[2] The structure of complex **11a** was determined crystallographically and is discussed later.

The pentaruthenium complexes **12** and **13** were isolated as green and dark red compounds, respectively. However, their spectroscopic data yielded little structural information, the IR spectrum of **12** having six bands due to terminal carbonyl units and that of **13** having seven, and in addition a stretch at 1954 cm^{-1} in the region expected for semi-bridging carbonyl ligands. The ^{1}H NMR spectrum of **12** indicated the presence of phenyl protons only (δ 7.36, m) which, in conjunction with an elemental analysis and mass spectrum, suggested that the compound



Scheme 3



Scheme 4 [Ru] = Ru(CO)$_3$.

was a pentaruthenium species containing a C_3Ph_2 unit and 15 terminal CO ligands. The corresponding data for complex **13** were indicative of a similar Ru_5 cluster containing a C_3(Me)Ph [δ 7.36, m, 5H; 2.36, s, 3H] ligand and terminal and semi-bridging carbonyls (15 in total). No satisfactory ^{13}C NMR spectra could be obtained for either complex due to the low yields of the clusters. The structures of **12** and **13** were eventually determined by single crystal X-ray diffraction studies and are discussed later.

Molecular structure of complex 11a

The structure of complex **11a** is shown in Fig. 1 and relevant bond lengths and angles in Table 3. The three ruthenium atoms form an isosceles triangle [Ru(1)–Ru(2) 2.7984(5), Ru(1)–Ru(3) 2.7672(7) and Ru(2)–Ru(3) 2.7669(8) Å], with each of the ruthenium atoms having three terminal carbonyl units co-ordinated. In addition, the Ru(1)–Ru(2) edge is bridged by a carbonyl ligand [Ru(1)–C(19) 2.225(2), Ru(2)–C(19) 2.107(2) Å]. Carbons C(1), C(2) and C(3) make up the C_3 backbone of a diphenyl substituted allenylidene unit which bridges all three ruthenium atoms, acting as a four-electron donor. Thus, C(1) is σ bound to Ru(1) and Ru(2) [Ru(1)–C(1) 2.0282(18), Ru(2)–C(1) 2.0702(19) Å] with the C(1)–C(2) bond co-ordinated in η^2 fashion to Ru(3) [Ru(3)-C(1) 2.1843(18), Ru(3)–C(2) 2.2498(18) Å]. This latter feature appears to have little effect upon the ligand bond lengths, with those of C(1)–C(2) [1.343(3) Å] and C(2)–C(3) [1.343(2) Å] being identical, but causes a bending of the ligand which has a C(1)–C(2)–C(3) angle of 150.49(19)°.

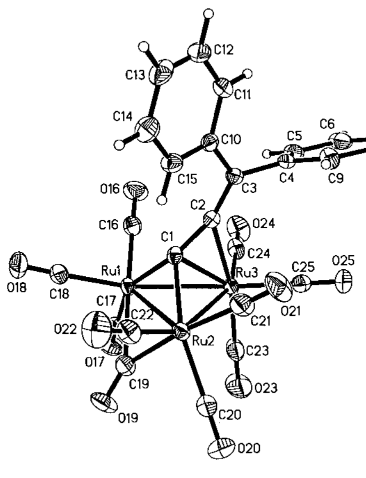


Fig. 1 Molecular geometry of complex **11a**, showing the labelling scheme.

These allenylidene dimensions correspond well with those seen for the analogous clusters $[Ru_3(CO)_7(\mu\text{-}CO)(\mu\text{-}dppm)(\mu_3\text{-}C{=}C{=}CPh_2)]$ **5**, $[Ru_3(CO)_9(\mu\text{-}H)(\mu\text{-}OMe)(\mu_3\text{-}C{=}C{=}CPh_2)]$, $[Ru_3(CO)_7(PPh_3)_2(\mu\text{-}H)(\mu\text{-}OH)(\mu_3\text{-}C{=}C{=}CPh_2)]$ and $[Ru_3(CO)_7(\mu\text{-}H)(\mu\text{-}OH)(\mu\text{-}dppm)(\mu_3\text{-}C{=}C{=}CPh_2)]$,[2,9] suggesting that substitution on the cluster has little effect.

The allenyidene complexes **11a**,**11b** are formed from **7a**,**7b** *via* loss of water from the bridging alkynol ligands. Comparison of this dehydration route with those previously seen for hydroxy-

Table 3 Selected bond lengths [Å] and angles [°] for complex **11a**

Ru(1)–C(1)	2.028(2)	Ru(3)–C(1)	2.184(2)
Ru(1)–C(19)	2.225(2)	Ru(3)–C(2)	2.250(2)
Ru(1)–Ru(3)	2.767(1)	C(1)–C(2)	1.343(3)
Ru(1)–Ru(2)	2.798(1)	C(2)–C(3)	1.343(2)
Ru(2)–Ru(3)	2.767(1)	C(3)–C(10)	1.491(3)
Ru(2)–C(1)	2.070(2)	C(3)–C(4)	1.492(3)
Ru(2)–C(19)	2.107(2)	C(19)–O(19)	1.144(2)
Ru(2)–Ru(1)–Ru(3)	59.62(2)	C(1)–Ru(3)–C(2)	35.21(7)
C(1)–Ru(1)–Ru(2)	47.57(5)	Ru(1)–C(1)–Ru(2)	86.12(7)
C(1)–Ru(1)–Ru(3)	51.42(5)	Ru(1)–C(1)–Ru(3)	82.04(6)
C(19)–Ru(1)–Ru(2)	47.95(6)	Ru(2)–C(1)–Ru(3)	81.09(7)
Ru(1)–Ru(2)–Ru(3)	59.63(2)	C(2)–C(1)–Ru(1)	134.36(15)
C(1)–Ru(2)–Ru(1)	46.31(5)	C(2)–C(1)–Ru(2)	127.25(14)
C(1)–Ru(2)–Ru(3)	51.25(5)	C(2)–C(1)–Ru(3)	75.06(11)
C(19)–Ru(2)–Ru(1)	51.63(6)	C(1)–C(2)–Ru(3)	69.73(11)
Ru(1)–Ru(3)–Ru(2)	60.75(2)	C(1)–C(2)–C(3)	150.49(19)
C(1)–Ru(3)–Ru(1)	46.54(5)	C(3)–C(2)–Ru(3)	138.35(15)
C(2)–Ru(3)–Ru(1)	76.08(5)	Ru(2)–C(19)–Ru(1)	80.42(7)
C(1)–Ru(3)–Ru(2)	47.66(5)	O(19)–C(19)–Ru(1)	136.14(18)
C(2)–Ru(3)–Ru(2)	74.80(5)	O(19)–C(19)–Ru(2)	143.43(18)

Table 4 Bond lengths [Å] and angles [°] for complex **12**

Ru(1)–Ru(2)	2.862(2)	Ru(3)–Ru(5)	2.8379(14)
Ru(1)–Ru(3)	2.814(1)	Ru(3)–C(16)	2.142(4)
Ru(1)–C(16)	2.401(4)	Ru(4)–Ru(5)	2.8082(15)
Ru(1)–C(17)	2.124(4)	Ru(4)–C(16)	2.106(4)
Ru(2)–Ru(3)	2.8194(12)	C(16)–C(17)	1.403(5)
Ru(2)–Ru(4)	2.7847(16)	C(17)–C(18)	1.360(5)
Ru(2)–Ru(5)	2.7934(12)	C(18)–C(25)	1.485(5)
Ru(2)–C(16)	2.113(4)	C(18)–C(19)	1.494(5)
Ru(3)–Ru(4)	2.786(3)		
Ru(2)–Ru(1)–Ru(3)	59.6(1)	C(16)–Ru(3)–Ru(2)	48.1(1)
C(16)–Ru(1)–Ru(2)	46.3(1)	C(16)–Ru(3)–Ru(4)	48.5(1)
C(16)–Ru(1)–Ru(3)	47.7(1)	C(16)–Ru(3)–Ru(5)	94.2(1)
C(17)–Ru(1)–Ru(2)	75.6(1)	Ru(2)–Ru(4)–Ru(3)	60.8(1)
C(17)–Ru(1)–Ru(3)	76.1(1)	Ru(2)–Ru(4)–Ru(5)	59.9(1)
C(17)–Ru(1)–C(16)	35.4(1)	Ru(3)–Ru(4)–Ru(5)	61.0(1)
Ru(1)–Ru(2)–Ru(3)	59.4(1)	C(16)–Ru(4)–Ru(2)	48.8(1)
Ru(1)–Ru(2)–Ru(4)	101.7(1)	C(16)–Ru(4)–Ru(3)	49.6(1)
Ru(1)–Ru(2)–Ru(5)	117.4(1)	C(16)–Ru(4)–Ru(5)	95.8(1)
Ru(3)–Ru(2)–Ru(4)	59.6(1)	Ru(2)–Ru(5)–Ru(4)	59.6(1)
Ru(3)–Ru(2)–Ru(5)	60.7(1)	Ru(2)–Ru(5)–Ru(3)	60.1(1)
Ru(4)–Ru(2)–Ru(5)	60.5(1)	Ru(3)–Ru(5)–Ru(4)	59.1(1)
C(16)–Ru(2)–Ru(1)	55.3(1)	C(17)–C(16)–Ru(2)	123.3(3)
C(16)–Ru(2)–Ru(3)	48.9(1)	C(17)–C(16)–Ru(4)	145.8(3)
C(16)–Ru(2)–Ru(4)	48.6(1)	Ru(1)–C(16)–Ru(2)	78.4(1)
C(16)–Ru(2)–Ru(5)	96.1(1)	Ru(1)–C(16)–Ru(3)	76.3(1)
Ru(1)–Ru(3)–Ru(2)	61.1(1)	Ru(1)–C(16)–Ru(4)	152.6(2)
Ru(1)–Ru(3)–Ru(4)	102.9(1)	Ru(2)–C(16)–Ru(3)	83.0(1)
Ru(1)–Ru(3)–Ru(5)	117.5(1)	Ru(2)–C(16)–Ru(4)	82.6(1)
Ru(2)–Ru(3)–Ru(5)	59.2(1)	Ru(3)–C(16)–Ru(4)	82.0(2)
Ru(2)–Ru(3)–Ru(4)	59.6(1)	C(17)–C(16)–Ru(1)	61.4(2)
Ru(4)–Ru(3)–Ru(5)	59.9(1)	C(17)–C(16)–Ru(3)	120.0(2)
C(16)–Ru(3)–Ru(1)	56.0(1)	C(16)–C(17)–Ru(1)	83.1(2)

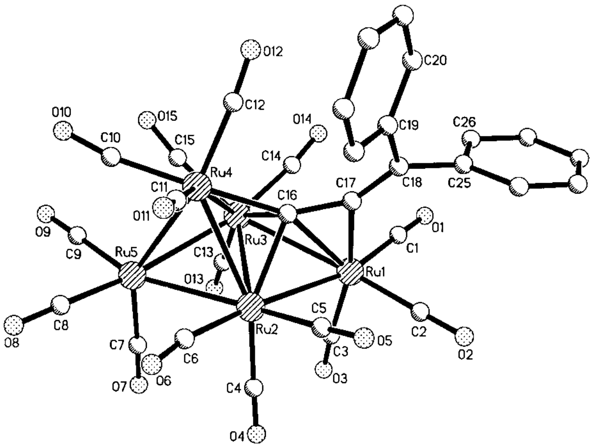


Fig. 2 Molecular geometry of complex **12**, showing the labelling scheme. All hydrogen atoms have been omitted for clarity.

alkynes at triiron, triruthenium and triosmium centres highlights some interesting points. As mentioned earlier, thermolysis of [Fe$_3$(CO)$_{12}$] in the presence of alkynols leads, in some cases, to spontaneous dehydration and formation of the corresponding allenylidene complex [Fe$_3$(CO)$_9$(μ-CO){μ_3-C=C=C(R)(R^1)}] **1**. These reactions were proposed to proceed *via* prior formation of a μ_3-(‖) alkynol species [Fe$_3$(CO)$_9$(μ-CO){μ_3-C(H)=CC(R)(R^1)OH}] which, under the reaction conditions, was never isolated (see Scheme 1).[5] Our observation that the acid induced dehydration of the analogous Ru$_3$ complexes [Ru$_3$(CO)$_9$(μ-CO){μ_3-C(H)=CC(R)OH(R^1)}] **7a**,**7b** affords the corresponding allenylidene species **11** lends some support to this hypothesis. That no such allenylidene ligands were formed upon addition of acid to the μ_3-(‖) osmium complexes [Os$_3$(CO)$_9$(μ-CO){μ_3-HC=CC(R)$_2$OH}] **9**[12] may be linked to the nature of the R substituents present. Thus, for our Ru$_3$ complexes, dehydration of **7a** ($R = R^1 =$ Ph) and **7b** (R = Ph, R^1 = Me) yielded allenylidene complexes, whereas protonation of **7c** ($R = R^1 =$ Me) or **7d** ($R = R^1 =$ H) gave unidentified cationic species only. The reactivity of the Os$_3$ complexes **9** towards acid was only studied for R = H or Me and also led to formation of cationic propargyl complexes [Os$_3$(CO)$_9$(μ-CO){μ_3-HC≡CC(R)$_2$}]$^+$ **10**. It appears that the presence of phenyl substituents on the alkynols in **7** is involved in determining whether or not formation of allenylidene complexes can occur. However, the number of phenyl groups also seems to be important; thus, the bis-phenyl substituted complex **7a** affords the corresponding allenylidene species **11a** in 70% yield but replacement of a phenyl with a methyl group (*i.e.* **7b**) lowers the yield of corresponding allenylidene complex **11b** to 59%. In addition, the nature of the non-phenyl substituent also plays a part, with substitution of the methyl group in **7b** for hydrogen (*i.e.* complex **7e**) preventing allenylidene formation completely.

The Introduction detailed how protonation of the propargyl alcohol derived alkynyl species [M$_3$(CO)$_9$(μ-H){μ_3-C$_2$C(Ph)$_2$-OH}] **2** (M = Ru or Os) led to the isolation of allenylidene complexes containing a range of substituents on the cluster edges. In contrast, the hydroxyalkyne species **7a** and **7b** have allowed us to isolate the ruthenium homologues of the triiron complexes [Fe$_3$(CO)$_9$(μ-CO){μ_3-C=C=C(R)(R^1)}] **1** for the first time. In addition, for the alkynyls **2** the presence of an alkyl group on the C–OH carbon prevented allenylidene formation, with dehydration yielding the corresponding ene-yne product **3** instead. As a result, the previously isolated Ru$_3$ and Os$_3$ allenylidene complexes have all contained the C=C=CR$_2$ (R = aryl) fragment. This is not the case for complexes **7**. Thus, dehydration of **7b** affords the first example of a triruthenium complex containing the unsymmetrically substituted C=C=C(Ph)Me ligand. Further, there is no experimental evidence for other dehydration pathways occurring leading to ene-yne formation.

Molecular structures of complexes 12 and 13

The structure of complex **12** is shown in Fig. 2 and relevant bond lengths and angles are presented in Table 4. Complex **12** contains an Ru$_5$ core with the atoms in an edge-bridged tetrahedral arrangement. The allenylidene unit (derived from dehydration of the hydroxyalkyne ligand in complex **7a**) interacts with one face [Ru-(2), -(3) and -(4)] of the tetrahedron and the edge-bridging Ru(1) atom. Thus, σ-type interactions are formed between the μ-carbido atom C(16) and the Ru(2)–(4) face [Ru(2)–C(16) 2.113(4), Ru(3)–C(16) 2.142(4) and Ru(4)–C(16) 2.106(4) Å]. This appears to be an overall two-electron donor interaction as the bond order of the C(16)–C(17) bond [length 1.403(5) Å] remains close to two, the moderate lengthening of this bond being attributed to the

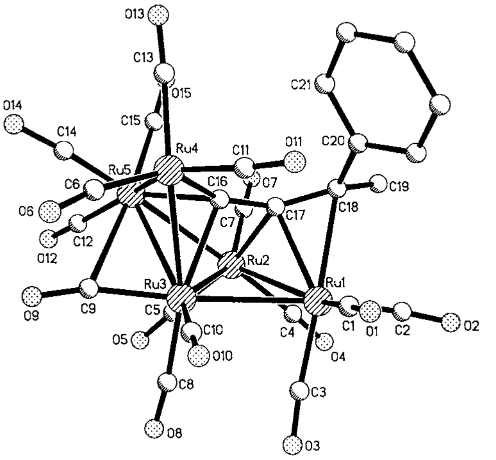


Fig. 3 Molecular geometry of complex **13**. Details as in Fig. 2.

π interaction it makes with Ru(1) [Ru(1)–C(16) 2.401(4), Ru(1)–C(17) 2.124(4) Å]. This co-ordination of C(16) to four ruthenium atoms is analogous to that seen for the corresponding C_α's of μ_4-carbene[1b] and μ_4-vinylidene[1a] complexes (*e.g.* [$Ru_4(CO)_{10}\{\mu_4\text{-C=C(H)Pr}^i\}(\mu_3\text{-OH})(\mu\text{-PPh}_2)$][17]). The C(17)–C(18) bond length [1.360(5) Å] of **12** suggests the presence of a localised double bond which remains unco-ordinated. Such an interaction of the allenylidene ligand through the C_α and C_β carbons only is similar to the bonding mode seen in complex **11a** and causes a bending of the ligand [C(16)–C(17)–C(18) 141.1(3)°] with the hybridisation of C(17) intermediate between sp and sp^2. Considering the μ_4-allenylidene fragment in **12** as a four-electron donor gives a cluster valence electron count of 74 in accord with the observed geometry which contains eight Ru–Ru bonds.

The structure of complex **13** is shown in Fig. 3 and relevant bond lengths and angles are presented in Table 5. The shape of the pentaruthenium core of **13** differs from that of **12**, the metal atoms now defining an edge-bridged butterfly, the shortest Ru(3)–Ru(5) vertex [2.7616(14) Å] being asymmetrically bridged by a carbonyl unit [Ru(3)–C(9) 1.902(13), Ru(5)–C(9) 2.579(12) Å; Ru(3)–C(9)–O(9) 163.4(10), Ru(5)–C(9)–O(9) 122.2(9)°]. Rutheniums (1), (2), (4) and (5) each have three terminally bound carbonyl ligands whereas Ru(3) has two. The hydrocarbon fragment of **13** is derived from the propargyl alcohol ligand of **7b** *via* loss of H and OH from carbons C(16) and C(18) respectively. The resulting allenylidene moiety bridges all five metal atoms, with σ-type interactions between the α-carbon [C(16)] and Ru(3), Ru(4) and Ru(5) [1.956(11)–2.187(10) Å], the β-carbon [C(17)] and Ru(2) [2.142(12) Å] and with the C(17)–C(18) bond co-ordinated in η^2 fashion to Ru(1) [Ru(1)–C(17) 2.206(10), Ru(1)–C(18) 2.410(12) Å]. A π co-ordination of the C_α–C_β bond was observed[3] for the analogous allenylidene ligand of the heptanuclear complex [$Ru_7(CO)_{19}\{\mu_4\text{-CC(H)C(O)Me}\}\{\mu_5\text{-CCC(H)Me}\}$] but a non-bonding Ru(2)···C(16) distance of 2.620 Å rules out such an interaction in **13**. The internal allenylidene bond lengths [C(16)–C(17) 1.405(13) and C(17)–C(18) 1.353(14) Å] are similar to those seen for the allenylidene unit of complex **12**; however, the bend in the ligand is much less [C(16)–C(17)–C(18) 136.1(11)°], possibly reflecting their different co-ordination modes. Co-ordination of the C_β–C_γ unsaturated bonds of bridging allenylidene ligands is rare and hence there are few examples of allenylidene units formally donating six electrons to the metal centre, the only other examples being the aforementioned heptanuclear species and the related propargyl complexes [$WRe_2(CO)_8(\mu\text{-OR})(\eta\text{-C}_5Me_5)(\mu_3\text{-C}\equiv\text{CCMe}_2)$][3] and [$Os_3(CO)_9(\mu\text{-H})(\mu_3\text{-C}\equiv\text{CCMe}_2)$].[12] The cluster valence count of **13** is 76, as expected for a Ru_5 cluster containing seven metal–metal bonds.

Table 5 Selected bond lengths [Å] and angles [°] for complex **13**

Ru(1)–C(17)	2.206(10)	Ru(3)–Ru(4)	2.8562(15)
Ru(1)–C(18)	2.410(12)	Ru(4)–C(16)	1.956(11)
Ru(1)–Ru(2)	2.8093(14)	Ru(4)–Ru(5)	2.7869(14)
Ru(1)–Ru(3)	2.8715(14)	Ru(5)–C(16)	2.131(10)
Ru(2)–C(17)	2.142(12)	Ru(5)–C(9)	2.579(12)
Ru(2)···C(16)	2.620(12)	C(9)–O(9)	1.155(12)
Ru(2)–Ru(3)	2.8179(14)	C(16)–C(17)	1.405(13)
Ru(2)–Ru(5)	2.8880(15)	C(17)–C(18)	1.353(14)
Ru(3)–C(9)	1.902(13)	C(18)–C(20)	1.499(15)
Ru(3)–C(16)	2.187(10)	C(18)–C(19)	1.542(13)
Ru(3)–Ru(5)	2.7616(14)		
C(17)–Ru(1)–C(18)	33.7(3)	C(9)–Ru(5)–Ru(3)	41.5(3)
C(17)–Ru(1)–Ru(2)	48.8(3)	C(16)–Ru(5)–Ru(4)	44.4(3)
C(18)–Ru(1)–Ru(2)	75.1(3)	Ru(3)–Ru(5)–Ru(4)	61.96(4)
C(17)–Ru(1)–Ru(3)	68.9(3)	C(16)–Ru(5)–Ru(2)	60.7(3)
C(18)–Ru(1)–Ru(3)	100.6(3)	Ru(3)–Ru(5)–Ru(2)	59.79(3)
Ru(2)–Ru(1)–Ru(3)	59.46(3)	Ru(4)–Ru(5)–Ru(2)	103.18(4)
C(17)–Ru(2)–C(16)	32.4(3)	O(9)–C(9)–Ru(3)	163.4(10)
C(17)–Ru(2)–Ru(1)	50.7(3)	O(9)–C(9)–Ru(5)	122.2(9)
C(16)–Ru(2)–Ru(1)	65.1(2)	Ru(3)–C(9)–Ru(5)	74.4(4)
C(17)–Ru(2)–Ru(3)	70.8(3)	C(17)–C(16)–Ru(4)	151.8(9)
C(16)–Ru(2)–Ru(3)	47.3(2)	C(17)–C(16)–Ru(5)	120.3(8)
Ru(1)–Ru(2)–Ru(3)	61.37(3)	Ru(4)–C(16)–Ru(5)	85.9(4)
C(17)–Ru(2)–Ru(5)	74.1(3)	C(17)–C(16)–Ru(3)	107.0(8)
C(16)–Ru(2)–Ru(5)	45.2(2)	Ru(4)–C(16)–Ru(3)	87.0(4)
Ru(1)–Ru(2)–Ru(5)	107.25(4)	Ru(5)–C(16)–Ru(3)	79.5(3)
Ru(3)–Ru(2)–Ru(5)	57.88(3)	C(17)–C(16)–Ru(2)	54.7(6)
C(9)–Ru(3)–Ru(5)	64.1(3)	Ru(4)–C(16)–Ru(2)	152.4(5)
C(16)–Ru(3)–Ru(5)	49.4(3)	Ru(5)–C(16)–Ru(2)	74.1(3)
C(16)–Ru(3)–Ru(2)	61.6(3)	Ru(3)–C(16)–Ru(2)	71.1(3)
Ru(5)–Ru(3)–Ru(2)	62.33(4)	C(18)–C(17)–C(16)	136.1(11)
C(16)–Ru(3)–Ru(4)	43.2(3)	C(18)–C(17)–Ru(2)	130.8(8)
Ru(5)–Ru(3)–Ru(4)	59.46(3)	C(16)–C(17)–Ru(2)	92.9(7)
Ru(2)–Ru(3)–Ru(4)	103.22(4)	C(18)–C(17)–Ru(1)	81.4(7)
C(16)–Ru(3)–Ru(1)	69.1(3)	C(16)–C(17)–Ru(1)	106.1(7)
Ru(5)–Ru(3)–Ru(1)	109.04(4)	Ru(2)–C(17)–Ru(1)	80.5(4)
Ru(2)–Ru(3)–Ru(1)	59.17(3)	C(17)–C(18)–C(20)	118.2(10)
Ru(4)–Ru(3)–Ru(1)	99.54(4)	C(17)–C(18)–C(19)	123.8(10)
C(16)–Ru(4)–Ru(5)	49.7(3)	C(20)–C(18)–C(19)	112.3(9)
C(16)–Ru(4)–Ru(3)	49.9(3)	C(17)–C(18)–Ru(1)	64.8(6)
Ru(5)–Ru(4)–Ru(3)	58.58(4)	C(20)–C(18)–Ru(1)	118.7(7)
C(16)–Ru(5)–Ru(3)	51.1(3)	C(19)–C(18)–Ru(1)	110.2(7)

The bonding modes of allenylidene seen in complexes **12** and **13** represent a new form of co-ordination for μ_5-allenylidene and the first example of a μ_4-allenylidene ligand. Overall, the formation of **12** and **13** from **7a** and **7b** respectively involves loss of water from C_α and C_γ of the alkynol ligands, cluster degradation and metal fragment condensation. However, it is not clear why the bonding modes of the allenylidene units or the geometries of the metal cores in **11** and **12** should vary according to the nature of the R substituent in complexes **7**, or why these complexes should be formed under the relatively mild reaction conditions used. It may be that steric effects play some role in the co-ordination modes of the allenylidene units. Thus, the presence of two bulky phenyl groups in **12** may disfavour co-ordination of C_γ. We are currently examining ways of improving the yields of complexes **12** and **13** to enable us to study any structural relationship between the two and to compare their reactivity. The unexpected formation of the complexes **11** in good yields from the μ_3-(||) hydroxyalkyne species **7a**,**7b** has allowed us to begin a study into the reactivity of such μ_3-allenylidene complexes towards small organic molecules with surprising initial results which will be described in a succeeding paper.

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 or alumina (Brockmann activity II). Reactions were routinely monitored by IR spectroscopy. Solution IR spectra were recorded on a Perkin-Elmer

1710 Fourier transform spectrometer using calcium fluoride cells of 1 mm path length, FAB mass spectra using a Fisons Autospec instrument and 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 alkynols and $HBF_4 \cdot OEt_2$ were used as supplied. The complex $[Ru_3(CO)_{10}(NCMe)_2]$ was prepared by the literature method.[10]

Formation of the hydroxyalkyne complexes $[Ru_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}C(H){=}CC(R)OH(R^1)\}]$ 7

The complexes **7** were all synthesized *via* the same general method. To a dichloromethane solution (50 cm^3) of freshly prepared $[Ru_3(CO)_{10}(NCMe)_2]$ (200 mg; 0.30 mmol) was added a 3-fold excess of the appropriate alkynol $HC{\equiv}CC(R)(R^1)OH$ (0.90 mmol) and the mixture stirred at room temperature for 10 min. An immediate change from yellow to red was observed. Removal of solvent and chromatography on silica gel, eluting with dichloromethane–hexane (1 : 1), gave the corresponding orange complex **7**. The products were further purified by recrystallisation from hexane at −20 °C. The yields of the complexes, after recrystallisation, were as follows: **7a** ($R = R^1 = Ph$) 68%; **7b** ($R = Ph, R^1 = Me$), **7c** ($R = R^1 = Me$) and **7d** ($R = R^1 = H$) 56%. Complex **7e** ($R = Ph, R^1 = H$) could only be obtained as an oil and so a yield was not calculated.

Decarbonylation of the hydroxyalkyne complexes $[Ru_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}C(H){=}CC(R)OH(R^1)\}]$ 7

(i) Thermally. Heating at reflux of a heptane solution (50 cm^3) of the μ_3-(||) alkynol species **7b** (100 mg) for 10 min resulted in a change from orange to yellow. Removal of solvent and chromatography on alumina afforded the corresponding alkynyl complex $[Ru_3(CO)_9(\mu\text{-}H)\{\mu_3\text{-}C_2C(Ph)OH(Me)\}]$ **8b** in a yield of 95%.

(ii) Using alumina. Chromatography of complexes **7a**–**7c** on alumina, eluting with hexane, resulted in isolation of small amounts of the starting complexes and the corresponding alkynyl species **8a**–**8c** in yields of 30–60%.

Protonation of $[Ru_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}C(H){=}CC(Ph)_2OH\}]$ 7a

To a dichloromethane solution (15 cm^3) of complex **7a** (0.36 g; 0.45 mmol) were added 2 drops of $HBF_4 \cdot OEt_2$ resulting in an immediate change from orange-red to purple. The solvent was removed, under reduced pressure, and the oily residue washed with diethyl ether (2 × 10 cm^3 portions). The remaining solid was then washed with hexane and the resulting purple solution decanted, filtered and chromatographed on alumina to afford the following bands: (i) purple, eluting with hexane, $[Ru_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}C{=}C{=}C(Ph)_2\}]$ **11a** (0.20 g, 70%); (ii) green, eluting with hexane, $[Ru_5(CO)_{15}(\mu_4\text{-}CC{=}CPh_2)]$ **12** (5%). Recrystallisation of complexes **11a** and **12** from heptane at −20 °C yielded crystals suitable for an X-ray diffraction study.

Protonation of $[Ru_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}C(H){=}CC(Ph)OH(Me)\}]$ 7b

To a dichloromethane solution (15 cm^3) of complex **7b** (0.43 g; 0.59 mmol) were added 2 drops of $HBF_4 \cdot OEt_2$ resulting in an immediate change from orange-red to purple. The solvent was removed, under reduced pressure, and the oily residue washed with diethyl ether (2 × 10 cm^3 portions). The remaining solid was then washed with hexane and the resulting purple solution decanted, filtered and chromatographed on alumina to afford the following bands: (i) purple, eluting with hexane, $[Ru_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}C{=}C{=}C(Ph)(Me)\}]$ **11b** (0.18 g, 59%); (ii) dark red, eluting with dichloromethane–hexane (1 : 49), $[Ru_5(CO)_{15}\{\mu_5\text{-}CC{=}C(Ph)Me\}]$ **13** (5%). Recrystallisation of complexes **11b** and **13** from heptane at −20 °C yielded crystals suitable for an X-ray diffraction study.

Table 6 Details of structure analysis for complexes **11a**, **12** and **13**

	11a	12	13
Formula	$C_{25}H_{10}O_{10}Ru_3$	$C_{30}H_{10}O_{15}Ru_5$	$C_{25}H_8O_{15}Ru_5$
M	773.54	1115.73	1053.66
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	*Pbca*
a/Å	10.205(2)	9.820(5)	21.794(3)
b/Å	11.178(2)	12.992(5)	16.8602(18)
c/Å	12.417(2)	14.957(5)	32.854(4)
α/°	73.38(1)	98.72(5)	
β/°	85.05(2)	104.12(6)	
γ/°	72.56(2)	110.94(4)	
U/Å^3	1294.9(4)	1667.2(12)	12073(3)
Z	2	2	16
μ/cm^{-1}	1.78	2.28	2.51
Total data	13596	17369	54677
Unique data	5860	7545	8923
R_{int} (%)	1.8	3.4	21
Observed data, N_o	5128	5893	4786
$R1$ (observed data) (%)	1.7	2.9	5.0
$wR2$ (all data) (%)	3.7	6.4	7.2

Crystal structure determinations of complexes 11a, 12 and 13

Single crystals of these compounds were all grown by cooling of a heptane solution of the appropriate complex to −20 °C. 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 6. Crystals of **13** were obtained as small, very thin plates (the crystal used had dimensions of 0.20 × 0.20 × 0.05 mm), and perhaps unsurprisingly the data obtained were very weak. The high value of R_{int} is a reflection of this.

CCDC reference number 186/2188.

See http://www.rsc.org/suppdata/dt/b0/b006146h/ for crystallographic files in .cif format.

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References

1 (*a*) M. I. Bruce, *Chem. Rev.*, 1991, **91**, 197; (*b*) W. A. Herrmann, *Adv. Organomet. Chem.*, 1982, **20**, 159; (*c*) E. Sappa, *J. Cluster. Sci.*, 1994, **5**, 211.

2 M. I. Bruce, *Chem. Rev.*, 1998, **98**, 2797.

3 C. S. Lau and W. T. Wong, *J. Chem. Soc., Dalton Trans.*, 1998, 3391.

4 H. Berke, U. Grossmann, G. Huttner and L. Zslona, *Chem. Ber.*, 1984, **117**, 3432.

5 E. Sappa, G. Predieri, A. Tiripicchio and F. Ugozzoli, *Gazz. Chim. Ital.*, 1995, **125**, 51.

6 G. Gervasio and E. Sappa, *Organometallics*, 1993, **12**, 1458.

7 (*a*) S. Aime, L. Milone and A. J. Deeming, *J. Chem. Soc., Chem. Commun.*, 1980, 1168; (*b*) S. Ermer, R. Karpelus, S. Miurs, E. Rosenberg, A. Tiripicchio and A. M. M. Lanfredi, *J. Organomet. Chem.*, 1980, **187**, 81; (*c*) G. Gervasio, R. Gobetto, P. J. King, D. Marabello and E. Sappa, *Polyhedron*, 1998, **17**, 2937.

8 S. Aime, A. J. Deeming, M. B. Hursthouse and J. D. Baker-Dirks, *J. Chem. Soc., Dalton Trans.*, 1982, 1625.

9 M. I. Bruce, B. W. Skelton, A. H. White and N. N. Zaitseva, *J. Chem. Soc., Dalton Trans.*, 2000, 881.

10 G. A. Foulds, B. F. G. Johnson and J. Lewis, *J. Organomet. Chem.*, 1985, **294**, 147; N. E. Leadbeater, *J. Organomet. Chem.*, 1999, **573**, 211.

11 S. Aime, R. Gobetto, L. Milone, D. Osella, L. Violano, A. J. Arce and Y. De Sanctis, *Organometallics*, 1991, **10**, 2854.

12 V. V. Krivykh, O. A. Kizas, E. V. Voronstov, F. M. Dolgushin, A. I. Yanovsky, Yu. T. Strunchkov and A. A. Koridze, *J. Organomet. Chem.*, 1996, **508**, 39.
13 P. J. King and E. Sappa, *J. Chem. Soc.*, *Dalton Trans.*, submitted for publication.
14 J. P. H. Charmant, G. Davies, P. J. King, J. R. Wigginton and E. Sappa, *Organometallics*, 2000, **19**, 2330.
15 G. Gervasio, D. Marabello and E. Sappa, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 1851.
16 O. A Kizas, V. V. Krivykh, E. V. Voronstov and A. A. Koridze, *Bull. Acad. Sci. USSR Div. Chem.* (*Engl. Transl.*), 1993, 1102.
17 A. J. Carty, S. A. MacLaughlin and N. J. Taylor, *J. Chem. Soc.*, *Chem. Commun.*, 1981, 476.