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Preparation and structural characterisation of some ruthenium cluster carbonyls containing allenylidene ligands†

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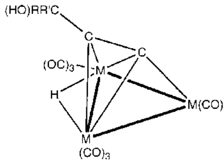
The chemistry of some ruthenium cluster carbonyls containing allenylidene ligands has been reinvestigated. Treatment of $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2CAr_2(OH)\}(CO)_9$ [Ar = Ph **15**, tol (tol = $4\text{-}MeC_6H_4$)] with $HBF_4{\cdot}OMe_2$ gave $Ru_3(\mu\text{-}H)(\mu_3\text{-}CCCAr_2)(CO)_9$ (Ar = Ph, R = H, Me; Ar = tol, R = H). Substitution of CO by PPh_3 or dppm gave $Ru_3(\mu\text{-}H)(\mu_3\text{-}CCCPh_2)(\mu\text{-}OH)(CO)_7(L)_2$ (L = PPh_3, L_2 = dppm; from **15**), while in the presence of HBF_4, the hydroxy-free complexes $Ru_3(\mu_3\text{-}CCCAr_2)(\mu\text{-}dppm)(\mu\text{-}CO)(CO)_7$ were obtained. Reactions of **15** with $K[BHBu^s_3]$, followed by HBF_4 or $AuCl(PPh_3)$, also resulted in loss of water to give $Ru_3(\mu\text{-}H)(\mu\text{-}E)(\mu_3\text{-}CCCPh_2)(CO)_9$ [E = H or $Au(PPh_3)$, respectively]. X-Ray structures of six of the complexes are reported.

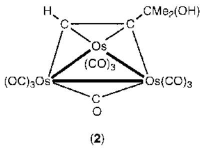
Introduction

The chemistry of unsaturated carbenes as ligands to metal centres continues to generate strong interest. The simplest unsaturated carbene is vinylidene, $:C{=}CH_2$, and a host of both mono- and polynuclear complexes have been described.[1] Complexes containing allenylidene, $:C{=}C{=}CH_2$, are well-established for mononuclear systems, but the chemistry of cluster complexes is far less well developed.[2] This is in spite of the first such complexes having been obtained over seventeen years ago.[3]

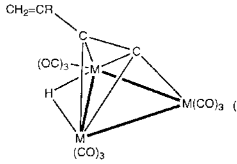
The common route to C_3 unsaturated carbenes is by loss of water or alcohol from an intermediate (and sometimes undetected) hydroxymethylvinylidene derivative. This reaction was first described for ruthenium in the synthesis of $[Ru(C{=}C{=}CPh_2)(PMe_3)_2Cp]^+$ from $RuCl(PMe_3)_2Cp$ and $HC{\equiv}CCPh_2(OH)$.[4] Reactions of propargyl alcohols with ruthenium and osmium cluster carbonyls were first described in 1980, when the complexes $M_3(\mu\text{-}H)\{\mu_3\text{-}C_2CRR'(OH)\}(CO)_9$ (**1**; M = Ru; R = Me, R′ = Me, Et, Ph) were obtained in 4, 58 and 33% yields, respectively, from $Ru_3(CO)_{12}$ and $HC{\equiv}CCRR'(OH)$.[5] Reactions of the related disubstituted alkynes $C_2\{CR_2(OH)\}_2$ (R = Me, Ph) with $M_3(CO)_{12}$ (M = Ru, Os) afforded **1** (R = R′ = Me, Ph) with loss of the corresponding ketone R_2CO; the ruthenium complexes were obtained in only low yields and were characterised spectroscopically, the major products being binuclear complexes, together with some 1,1,4,4-tetraphenylbutadiene from R = R′ = Ph.[6,7] The reactions of $Ru_3(CO)_{12}$ have been examined again recently, with similar results, examples of **1** (M = Ru) with R = Me, R′ = Me, Et, Pr, Ph and R = R′ = Ph being described.[8] Reactions of $HC{\equiv}CCH_2(OH)$ or $C_2\{CH_2(OH)\}_2$ afforded a variety of other structural types; with $Os_3(\mu\text{-}H)_2(CO)_{10}$, the alkyne cluster $Os_3\{\mu_3\text{-}HC_2CMe_2(OH)\}(\mu\text{-}CO)(CO)_9$ (**2**) was obtained in 66% yield, which on heating was converted into $Os_3(\mu\text{-}H)\{\mu_3\text{-}C_2CMe_2(OH)\}(CO)_9$ (**3**) in 83% yield.[5]



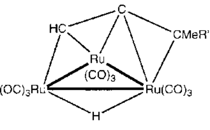
(**1**)
(**3**) M = Os, R = R′ = Me



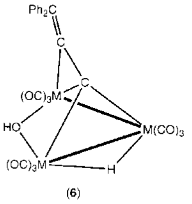
(**2**)



(**4**)



(**5**)



(**6**)

Treatment of the hydrido–alkynyl complexes with strong acids (CF_3CO_2H or H_2SO_4) or on TLC silica resulted in dehydration to give the vinylalkynyl clusters $M_3(\mu\text{-}H)(\mu_3\text{-}C_2CR{=}CH_2)(CO)_9$ (**4**; M = Ru, Os; R = H, Me, Ph). Dehydration also occurred during the reaction of $Ru_3(CO)_{12}$ and $HC{\equiv}CCMeR'(OH)$ (R′ = Me, Ph) with KOH in methanol, when the allenyl complexes $Ru_3(\mu\text{-}H)(\mu_3\text{-}CH{=}C{=}CMeR')$ $(CO)_9$(**5**) were obtained.[9]

When R = R′ = Ph, however, treatment with CF_3CO_2H resulted in migration of the OH group to the cluster to give the allenylidene complexes $M_3(\mu\text{-}H)$ $(\mu_3\text{-}CCCPh_2)(\mu\text{-}OH)(CO)_9$ (**6**; M = Ru, Os), of which the osmium complex was structurally characterised to show the allenylidene attached to the cluster by two carbons in the $\mu_3\text{-}\eta^1:\eta^1:\eta^2$ mode.[3] The ruthenium analogue was identified spectroscopically. Other examples of cluster-bound allenylidenes have been described.[2] Protonation of $Os_3\{\mu_3\text{-}HC_2CR_2(OH)\}(\mu\text{-}CO)(CO)_9$ (R = H, Me) is thought to produce clusters containing $\mu_3\text{-}\eta^1:\eta^2:\eta^3$-allenylidene ligands,[10] similar to those structurally characterised in $Re_2W(\mu_3\text{-}CCCMe_2)(\mu\text{-}OR)(CO)_8Cp^*$ (R = Me, Et, Ph).[11] In an Ru_7 complex isolated from reactions between $Ru_3(CO)_{12}$ and $HC{\equiv}CCHMe(OH)$, the allenylidene ligand is coordinated to five of the metal atoms in the $\eta^1:\eta^1:\eta^1:\eta^1:\eta^2$ mode.[12]

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† Dedicated to Professor Heinrich Vahrenkamp, a valued colleague and friend, on the occasion of his 60th birthday.

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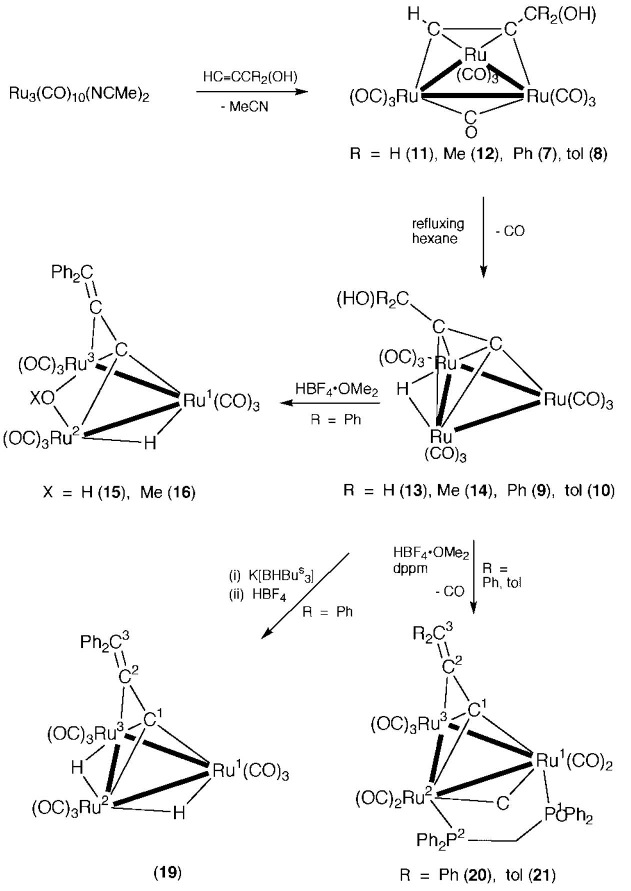


Scheme 1

This paper describes the preparation and structural characterisation of a variety of allenylidene complexes containing Ru_3 cores and provides a background to several recent preliminary accounts of further reactions of these complexes.[13]

Results

Alkyne and hydrido–alkynyl complexes

As with the earlier studies, we decided to use hydroxymethyl-1-alkynes as precursors for the allenylidene ligands. In contrast to previous studies summarised above, we have used $Ru_3(CO)_{10}(NCMe)_2$ as the source of the Ru_3 cluster, which reacts under milder conditions thereby enabling the isolation of the precursor complexes in much higher yields (Scheme 1). Thus, the reactions between $HC{\equiv}CCAr_2(OH)$ and $Ru_3(CO)_{10}(NCMe)_2$ afforded orange $Ru_3\{\mu_3\text{-}HC_2CAr_2(OH)\}(\mu\text{-}CO)(CO)_9$ [Ar = Ph (**7**), tol (**8**)] in 74 and 79% yields respectively. The diphenyl derivative **7** has been described before,[3] but the di-4-tolyl complex **8** is new. They were characterised by elemental analyses and from their spectroscopic properties (Table 1). Thus, their IR spectra contain terminal $\nu(CO)$ bands between 2097 and 1989 cm^{-1} and a characteristic bridging $\nu(CO)$ absorption near 1878 cm^{-1}, while the $\nu(OH)$ bands are found near 3605 cm^{-1}. In their ^1H NMR spectra, the acetylenic protons are found at δ 7.68 and 7.76, respectively, while in **8**, there are two singlet resonances for the Me groups at δ 2.24 and 2.37. The OH proton was found at δ 2.83 for **8**. The electrospray (ES) mass spectra contain $[M - H]^-$ at *m*/*z* 792 (for **7**) or $[M - 2H]^-$ at *m*/*z* 819 (for **8**).

Mild heating (refluxing hexane, 15 min) results in decarbonylation and formation of the hydrido–alkynyl complexes $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2CAr_2(OH)\}(CO)_9$ [Ar = Ph (**9**), tol (**10**)]. Again, **9** has been reported on an earlier occasion.[3] The IR spectra contain only terminal $\nu(CO)$ bands between 2099 and 1955 cm^{-1}, with $\nu(OH)$ absorptions near 3610 cm^{-1}. In the ^1H NMR spectra, the Ru–H singlet resonance occurs at δ −21.09 and −21.11, respectively, and the OH proton is at δ 2.58 in **10**; phenyl proton multiplets are between δ 7.27 and 7.80. For **10**, the Me groups give a singlet at δ 2.29. The ES mass spectra contain $[M - H]^-$ at *m*/*z* 764 (for **9**) and M^- at *m*/*z* 793 (for **10**).

As mentioned above, formation of these complexes is not limited to aryl-substituted propyn-1-ols. Thus, we have observed that reactions between $Ru_3(CO)_{10}(NCMe)_2$ and $HC{\equiv}CCR_2(OH)$ ($R_2 = H_2$, HMe, Me_2) proceed readily under ambient conditions to give the corresponding alkyne clusters, of which we have isolated and characterised $Ru_3\{\mu_3\text{-}HC_2CR_2(OH)\}(\mu\text{-}CO)(CO)_9$ [R = H (**11**), Me (**12**)]; the mono-methyl complex was identified spectroscopically. Spectroscopic properties are consistent with the formulations. Thus, the terminal $\nu(CO)$ bands are between 2098 and 1985 cm^{-1} and the bridging $\nu(CO)$ absorption is near 1881 cm^{-1}; $\nu(OH)$ bands are at 3631 and 3602 cm^{-1}, respectively. In the ^1H NMR spectrum, the acetylenic protons are found at δ 8.30 and 8.22, respectively, with the CH_2 or CMe_2 protons at δ 4.20 and 1.36. The CMe_2 carbons are found at δ 35.02 (Me) and 77.42, respectively, in the ^{13}C NMR spectrum of **12**, while only one of the C_α and C_β resonances was seen at δ 137.84.

Thermolysis afforded the corresponding hydrido–alkynyl clusters $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2CR_2(OH)\}(CO)_9$ [R = H (**13**), Me (**14**)], identification also being largely spectroscopic, with a relatively imprecise X-ray structure determination confirming the broad structural features of **13** (see below). Only terminal $\nu(CO)$ bands are found between 2100 and 1957 cm^{-1} in their IR spectra, while in the ^1H NMR spectra the cluster-bonded protons are at δ −21.10 and −20.99, respectively, in **13** and **14**. The CH_2 and Me protons are found at δ 4.86 (in **13**) and as two singlets at δ 1.70 and 1.72 (in **14**). Recently, it was reported that reactions of $Ru_3(CO)_{12}$ with $HC{\equiv}CCRR'(OH)$ ($RR' = Me_2$,[12] MeEt,[12,13] MePr,[14] HEt[14]) in refluxing toluene afforded the corresponding hydrido–alkynyl complexes directly. The ^{13}C NMR spectrum of **14** contains resonances at δ 34.79 (Me), 70.38 (CMe_2), 106.99 (C_β) and 167.07 (C_α).

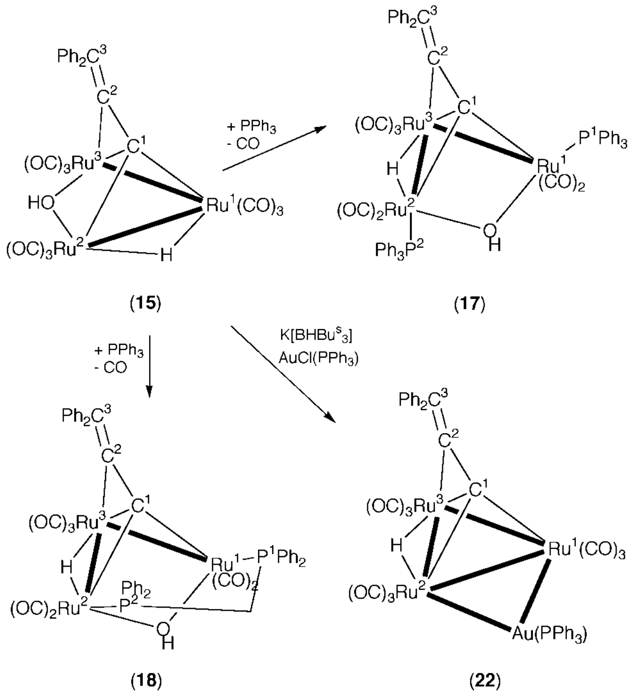
Allenylidene complexes

Treatment of a solution of **9** in CH_2Cl_2 with $HBF_4{\cdot}OMe_2$ results in a deepening of the colour. Conventional work-up afforded two complexes, which were identified as $Ru_3(\mu\text{-}H)(\mu_3\text{-}CCCPh_2)(\mu\text{-}OR)(CO)_9$ [R = H (**15**), Me (**16**)]. The former was described in the earlier study but not fully characterised.[3] Elemental analyses confirmed the formulations, with the ES mass spectrum of **15** containing an M^- ion at *m*/*z* 765. In their IR spectra, only terminal $\nu(CO)$ bands were found between 2101 and 1994 cm^{-1}. For **15**, a $\nu(OH)$ absorption was present at 3632 cm^{-1}. In the ^1H NMR spectra, Ru–H resonances were found at δ −11.13 and −10.80 for **15** and **16**, respectively, while the OMe singlet for **16** occurred at δ 3.03. Multiplets between δ 7.13 and 7.84 arise from the phenyl protons. Finally, a single crystal X-ray structure determination confirmed the identity of **16** (see below).

Substitution of CO groups occurs readily when **15** is heated with tertiary phosphines in refluxing toluene (Scheme 2). With PPh_3, two equatorial CO ligands on the Ru atoms bridged by the OH groups are replaced to give $Ru_3(\mu\text{-}H)(\mu_3\text{-}CCCPh_2)(\mu\text{-}OH)(CO)_7(PPh_3)_2$ (**17**), identified from a single-crystal X-ray structure determination (see below). Interestingly, subtle alterations in the structures of the substituted complexes have occurred, so that the OH group is opposite, rather than adjacent, to the allenylidene ligand. This may be a solid-state effect, reflecting a lower energy conformation; solubility considerations have precluded a variable temperature NMR study to determine whether the allenylidene ligand rotates around the Ru_3 core, as might be expected. The spectral properties were in accord with the solid-state structure, with only terminal $\nu(CO)$ bands found in the IR spectrum between 2062 and 1943 cm^{-1}, the Ru–H resonance at δ − 13.16 being a doublet (J_{HP} 10 Hz) as a result of coupling to the phosphorus atom attached to Ru(2).

Table 1 Analytical and spectroscopic data for some complexes

Complex	IR (cyclohexane/cm^{-1})	NMR (CDCl$_3$; δ, J/Hz)	ES mass spectra (m/z)
7 $Ru_3\{\mu_3\text{-}HC_2CPh_2(OH)\}(\mu\text{-}CO)(CO)_9$ Found: C, 38.28; H, 1.65. $C_{25}H_{12}O_{11}Ru_3$ calc.: C, 37.93; H, 1.53%; M, 793	ν(OH) 3602vw ν(CO) 2097m, 2062vs, 2053vs, 2029s, 2010m, 1879m(br)	^{1}H: 7.25–7.46 (m, 10H, 2Ph), 7.68 (s, 1H, HC≡)	(MeOH, negative ion): 792, $[M - H]^-$, 764, 680, 652, 624 $[M - H - n\text{CO}]^-$ (n = 1, 4–6); 580, $[M - OH - 7CO]^-$; 551, 474 $[Ru_3(C_3Ph_n)(CO)_2]^-$ (n = 2,1)
8 $Ru_3\{\mu_3\text{-}HC_2C(tol)_2(OH)\}(\mu\text{-}CO)(CO)_9$ Found: C, 39.69; H, 2.01. $C_{27}H_{16}O_{11}Ru_3$ calc.: C, 39.56; H, 1.95%; M, 821	ν(OH) 3607w ν(CO) 2096m, 2074m, 2061vs, 2053vs, 2028s, 2009m, 1989w, 1878m (br)	^{1}H: 2.24, 2.37 (2 × s, 2 × 3H, 2 × Me), 2.83 (s, 1H, OH), 6.70–7.25 (m, 8H, C_6H_4), 7.76 (s, 1H, HC≡)	(MeOH, negative ion): 819, $[M - 2H]^-$; 781–623, $[M - 2H - n\text{CO}]^-$ (n = 1–7); 577–493 $[M - 2H - m\text{CO} - Me_2O]^-$ (m = 7–10).
9 $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2CPh_2(OH)\}(CO)_9$ Found: C, 37.73; H, 1.58. $C_{24}H_{12}O_{10}Ru_3$ calc.: C, 37.75; H, 1.57%; M, 765	ν(OH) 3609vw ν(CO) 2099m, 2074vs, 2054vs, 2025vs, 1990m, 1972vw, 1958w	^{1}H: −21.09 (s, 1H, Ru–H), 7.27–7.80 (m, 10H, 2Ph)	(MeOH, negative ion): 764, $[M - H]^-$; 736–596, $[M - H - n\text{CO}]^-$ (n = 1–6); 551–495, $[M - H_2O - n\text{CO}]^-$ (n = 7–9)
10 $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2C(tol)_2(OH)\}(CO)_9$ Found: C, 39.49; H, 2.06. $C_{26}H_{16}O_{10}Ru_3$ calc.: C, 39.44; H, 2.02%; M, 793	ν(OH) 3610w ν(CO) 2099m, 2074vs, 2054vs, 2024vs, 1989m, 1970vw, 1955vw	^{1}H: −21.11 (s, 1H, Ru–H), 2.29 (s, 6H, 2Me), 2.58 (s, 1H, OH), 7.37 [dd, J(HH) 8.4, 8H, C_6H_4]	(MeOH, negative ion): 793, M^-; 764–596, $[M - H - n\text{CO}]^-$ (n = 1–7)
11 $Ru_3\{\mu_3\text{-}HC_2CH_2(OH)\}(\mu\text{-}CO)(CO)_9$ Found: C, 24.59; H, 0.68. $C_{13}H_4O_{11}Ru_3$ calc.: C, 24.41; H, 0.63%; M, 641	ν(OH) 3631vw ν(CO) 2098w, 2073w, 2060s, 2054vs, 2029s, 2009m, 1991vw, 1882w(br)	^{1}H: 4.20 [d, J(HH) 4, 2H, CH_2], 8.30 (s, 1H, HC≡)	(MeOH, negative ion): 639, $[M - 2H]^-$; 611–415, $[M - 2H - n\text{CO}]^-$ (n = 1–8)
12 $Ru_3\{\mu_3\text{-}HC_2CMe_2(OH)\}(\mu\text{-}CO)(CO)_9$ Found: C, 26.98; H, 1.28. $C_{15}H_8O_{11}Ru_3$ calc.: C, 26.99; H, 1.20%; M, 669	ν(OH) 3602w ν(CO) 2097m, 2060s, 2057vs, 2028s, 2007m, 1985 (sh), 1881w(br)	^{1}H: 1.36 (s, 6H, 2Me), 8.22 (s, 1H, HC≡) ^{13}C: 35.02 (s, 2 × Me), 77.42 (s, CMe_2), 137.84 (s, C_α, C_β), 191.61, 197.19 (2 × s, CO)	(MeOH, negative ion): 668, $[M - H]^-$; 640, $[M - H - CO]^-$; 582, 554, 526, $[M - 3H - n\text{CO}]^-$ (n = 3–5)
13 $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2CH_2(OH)\}(CO)_9$ Found: C, 23.57; H, 0.66. $C_{12}H_4O_{10}Ru_3$ calc.: C, 23.57; H, 0.65%; M, 613	ν(OH) 3621vw ν(CO) 2100w, 2073s, 2057s, 2024vs, 1992m, 1971vw, 1960vw	^{1}H: −21.10 (s, 1H, Ru–H), 4.86 [d, J(HH) 4.4, 2H, CH_2]	(MeOH, negative ion): 612, $[M - H]^-$, 583–415, $[M - 2H - n\text{CO}]^-$ (n = 1–7)
14 $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2CMe_2(OH)\}(CO)_9$ Found: C, 26.39; H, 1.26. $C_{14}H_8O_{10}Ru_3$ calc.: C, 26.29; H, 1.25%; M, 641	ν(OH) 3615w ν(CO) 2099w, 2072s, 2055vs, 2021s, 1989m, 1957vw	^{1}H: −20.99 (s, 1H, Ru–H), 1.70 (s, 3H, Me), 1.72 (s, 3H, Me) ^{13}C: 34.79 (s, 2Me), 70.38 (s, CMe_2), 106.99 (s, C_β), 167.07 (s, C_α), 188.36, 188.55, 197.07 (3 × s, CO)	(MeOH, negative ion): 640, $[M - H]^-$; 612, $[M - H - CO]^-$, 582, 554, 526, $[M - 3H - n\text{CO}]^-$ (n = 2–4)
15 $Ru_3(\mu\text{-}H)(\mu_3\text{-}CCCPh_2)(\mu\text{-}OH)(CO)_9$ Found: C, 37.49; H, 1.62. $C_{24}H_{12}O_{10}Ru_3$ calc.: C, 37.75; H, 1.57%; M, 765	ν(OH) 3632w ν(CO) 2103w, 2083s, 2062vs, 2040m, 2024 (sh), 2017s, 1994w	^{1}H: −11.13 (s, 1H, Ru–H), 7.13–7.43 (m, 10H, 2Ph)	(MeOH, negative ion): 765, M^-; 748, $[M - OH]^-$; 720, $[M - OH - CO]^-$
16 $Ru_3(\mu\text{-}H)(\mu_3\text{-}CCCPh_2)(\mu\text{-}OMe)(CO)_9$ Found: C, 38.90; H, 1.90. $C_{25}H_{14}O_{10}Ru_3$ calc.: C, 38.61; H, 1.80%; M, 779	ν(CO) 2101w, 2082s, 2073 (sh), 2061vs, 2051 (sh), 2038m, 2023 (sh), 2019s, 1994w	^{1}H: −10.80 (s, 1H, Ru–H), 3.03 (s, 3H, OMe), 7.55–7.84 (m, 10H, 2Ph)	
17 $Ru_3(\mu\text{-}H)(\mu_3\text{-}CCCPh_2)(\mu\text{-}OH)(CO)_7(PPh_3)_2$ Found: C, 55.99; H, 3.52. $C_{58}H_{42}O_8P_2Ru_3$ calc.: C, 56.55; H, 3.41%; M, 1233	ν(OH) 3612w ν(CO) 2062vs, 2043w, 2027m, 2009s, 1998s, 1981m, 1969m, 1963 (sh), 1943m	^{1}H: −13.16 [d, J(HP) 10, 1H, Ru–H], 6.89–7.59 (m, 40H, 8Ph)	
18 $Ru_3(\mu\text{-}H)(\mu_3\text{-}CCCPh_2)(\mu\text{-}OH)(\mu\text{-}dppm)(CO)_7$ Found: C, 50.11; H, 3.22. $C_{47}H_{34}O_8P_2Ru_3.0.5CH_2Cl_2$ calc.: C, 50.27; H, 3.08%; M, 1093	ν(OH) 3626w ν(CO) 2063vs, 2029vs, 2008s, 19986 (sh), 1980s, 1975 (sh), 1944m, 1924w	^{1}H: −5.56 [d, J(HP) 2.5, 1H, Ru–H], 3.76, 4.26 (2 × m, 2 × 1H, CH_2), 7.10–8.01 (m, 6Ph)	(MeOH, negative ion): 1126, $[M + MeOH + H]^-$; 1098–1014, $[M + MeOH + H - n\text{CO}]^-$ (n = 1–4)
19 $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}CCCPh_2)(CO)_9$	ν(CO) 2106w, 2094w, 2083m, 2073s, 2063m, 2052s, 2046m, 2033w, 2024vs, 2008w, 1988w	^{1}H: −20.95 (s, 2H, Ru–H), 7.12–8.53 (m, 10H, 2Ph)	
20 $Ru_3(\mu_3\text{-}CCCPh_2)(\mu\text{-}dppm)(\mu\text{-}CO)(CO)_7$ Found: C, 51.83; H, 2.99. $C_{48}H_{32}O_8P_2Ru_3$ calc.: C, 52.32; H, 2.91%; M, 1103	ν(CO) 2059s, 2027m, 2017(sh), 1999vs, 1974w, 1859w(br)	^{1}H: 2.88 [dt, J(HH) 13, J(HP) 11, 1H, CH_2], 3.36 [dt, J(HH) 13, J(HP) 11, 2H, CH_2], 7.19–7.33 (m, 30H, 6Ph) ^{13}C: 34.70 [t, J(CP) 37, CH_2P_2], 115.31 (s, C_γ0), 125.99–138.62 (m, Ph), 143.83 (s, C_β), 169.16 (s, C_α), 215.93, 227.93 (2 × s, CO)	(MeOH, negative ion): 1102, $[M - H]^-$; 1074–906, $[M - H - n\text{CO}]^-$ (n = 1–7); 884, $[Ru_3(CO)_7(dppm) - H]^-$
21 $Ru_3\{\mu_3\text{-}CCC(tol)_2\}(\mu\text{-}dppm)(\mu\text{-}CO)(CO)_7$ Found: C, 52.57; H, 3.16. $C_{50}H_{36}O_8P_2Ru_3$ calc.: C, 53.14; H, 3.21%; M, 1131	ν(CO) 2075vw, 2058s, 2026m, 2014 (sh), 1998vs, 1974w, 1858w	^{1}H: 2.37 (s, 6H, 2Me), 2.88, 3.39 (2 × m, 2 × 1H, CH_2), 7.11–7.35 (m, 28H, C_6H_4 + Ph)	(MeOH, negative ion): 1130, $[M - H]^-$; 1073–961, $[M - 2H - n\text{CO}]^-$ (n = 2–6)
22 $AuRu_3(\mu\text{-}H)(\mu_3\text{-}CCCPh_2)(CO)_9(PPh_3)$ Found: C, 41.74; H, 2.29. $C_{42}H_{25}AuO_9PRu_3$ calc.: C, 41.87; H, 2.09%; M, 1207	ν(CO) 2081w, 2076w, 2060m, 2054vs, 2039s, 2028s, 2005m, 1985m, 1979 (sh), 1964m	^{1}H: −20.47 [d, J(HP) 7, 1H, Ru–H], 7.12–7.45 (m, 25H, 5Ph)	(MeOH + NaOMe, negative ion): 1238, $[M + OMe]^-$; 1207, M^-; 1179, 1151, $[M - n\text{CO}]^-$ (n = 1, 2); 917–805, $[M - PPh_3 - n\text{CO}]^-$ (n = 1–5)



Scheme 2

A similar complex, $Ru_3(\mu\text{-}H)(\mu_3\text{-}CCCPh_2)(\mu\text{-}dppm)(\mu\text{-}OH)(CO)_7$ (**18**) was obtained with dppm, this ligand bridging the same rutheniums as are coordinated to PPh_3 ligands in **17**. In **18**, the ν(CO) bands are between 2063 and 1924 cm^{-1} and ν(OH) at 3626 cm^{-1}. The ^1H NMR spectrum contains a doublet Ru–H resonance at δ −5.56 [*J*(HP) 2.5 Hz] and the dppm CH_2 group gives rise to two multiplets at δ 3.76 and 4.26.

In seeking to find a route to cluster complexes containing allenylidene ligands free from other functional groups such as OH or OMe, we treated **9** with $K[BHBu^s{}_3]$, followed by HBF_4, *i.e.* with H^-/H^+(Scheme 1). Separation of the products afforded a small amount of the hydrido–allenylidene complex $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}CCCPh_2)(CO)_9$ (**19**), accompanied by some $Ru_4(\mu\text{-}H)_4(CO)_{12}$ and $Ru_4(\mu\text{-}H)_2(CO)_{13}$, the latter identified crystallographically. The IR spectrum of **19** contained ν(CO) bands between 2106 and 1988 cm^{-1}, indicating that no bridging CO groups were present. The ^1H NMR spectrum contained an Ru–H resonance at δ −20.95 together with phenyl multiplets between δ 7.12 and 8.53. The structure of **19** was confirmed by an X-ray determination (see below).

In the presence of dppm, protonation of **9** or **10** afforded hydroxyl-free phosphine-substituted complexes. With dppm and HBF_4, the complexes $Ru_3(\mu_3\text{-}CCCAr_2)(\mu\text{-}dppm)(\mu\text{-}CO)(CO)_7$ [Ar = Ph (**20**), tol (**21**)] were obtained. The dppm complexes were identified from elemental analyses and their ES mass spectra initially, together with an X-ray structure determination. The IR spectra contained ν(CO) bands between 2075 and 1974 cm^{-1} and bridging ν(CO) absorptions near 1859 cm^{-1}. In the ^1H NMR spectrum, the CH_2 proton multiplets are near δ 2.88 and 3.36, while for **21**, the Me resonance was at δ 2.37. No high-field resonance attributable to Ru–H is present. The ^{13}C NMR spectrum of **21** singlet resonances for the CH_2 carbon at δ 34.70 and for C_α, C_β and C_γ at δ 169.16, 143.83 and 115.31, respectively. In the ES mass spectrum of **20**, $[M - H]^-$ is at *m*/*z* 1102.

Auration of **15** by successive reactions with $K[BHBu^s{}_3]$ and $AuCl(PPh_3)$ also resulted in loss of the cluster-bound OH group and formation of $AuRu_3(\mu\text{-}H)(\mu_3\text{-}CCCPh_2)(CO)_9(PPh_3)$ (**22**; Scheme 2), a complex that is isolobal with **19**. This compound was initially characterised from a single-crystal X-ray study (see below). The spectral properties are consistent with the solid-state structure, with terminal ν(CO) bands between 2081 and 1964 cm^{-1} in its IR spectrum, the Ru–H doublet resonance at δ −20.47 in the ^1H NMR spectrum, together with the expected phenyl multiplets, and $[M + OMe]^-$ and M^- at *m*/*z* 1238 and 1207, respectively, in the ES mass spectrum of a solution containing NaOMe.

Molecular structures

Molecules of each of complexes **16**–**22** are portrayed in Fig. 1 and Fig. 2 and significant structural parameters are collected in Table 2. The common numbering system has been chosen so that C(1) of the allenylidene ligand caps the Ru_3 triangle with the C(1)–C(2) moiety being attached to Ru(3) in all cases. The Ru(1)–Ru(2) vector is bridged by H (**16**, **19**), OMe (**17**), OH + dppm (**18**), CO + dppm (**20**, **21**) or $Au(PPh_3)$ groups (**22**).

Complexes **16**–**18** have 50 cluster valence electrons (c.v.e.), two more than the 48 c.v.e. required for an M_3 cluster with three M–M bonds. Consequently, a bent Ru_3 geometry is adopted, with the Ru···Ru vector being non-bonded [Ru···Ru separations are between 3.194(2) and 3.3198(7) Å]. This non-bonded vector is bridged by the OH or OMe groups and in **17** or **18**, these two metal atoms are the sites of attachment of the tertiary phosphine ligands. In **18**, therefore, atoms Ru(1) and Ru(2) are also bridged by the dppm ligand. The relative positions of the allenylidene and OX ligands in these three complexes has changed as a result of rotation of the allenylidene ligand, atoms C(1)–C(2) moving from the terminal Ru (also bonded to O) in **16** to the central Ru of the Ru_3 chain in **17** and **18**. It is likely that this occurs as a result of steric interactions between the respective phenyl groups on the tertiary phosphines and the allenylidene ligands, resulting in migration of the latter ligand around the cluster. Although we have as yet no evidence for this process in **15** or **16**, for example, similar processes are common for cluster-bonded vinylidenes.

The separations of bonded pairs of Ru atoms range from 2.7519(5) to 2.920(1) Å. Those bridged only by C(1) are between 2.7519(5) and 2.887(1) Å. If a hydrogen bridges the bond, the separation is generally lengthened as expected, although the range is between 2.7389(9) and 2.920(1) Å. The distance Ru(1)–Ru(2) is generally shorter [2.7839(9)–2.8418(7) Å] than between Ru(1 or 2)–Ru(3) [2.847(1)–2.920(1) Å]. In **20** or **21**, the Ru(1)–Ru(2) bonds are bridged by CO and dppm and are 2.7863(6) and 2.7728(4) Å, respectively. In **22**, Ru(1)–Ru(2) is bridged by $Au(PPh_3)$ and is 2.891(1) Å.

Atom C(1) is σ-bonded to Ru(1) and Ru(2) [range 2.002(5)–2.10(1) Å], while the C(1)–C(2) moiety is π-bonded to Ru(3) [ranges Ru(3)–C(1) 2.16(1)–2.262(5) Å; Ru(3)–C(2) 2.223(5)–2.29(1) Å]. The C(1)–C(2) and C(2)–C(3) separations somewhat surprisingly, are similar [1.32(2)–1.35(2) and 1.31(2)–1.357(6) Å]. The attachment of the allenylidene ligand to the cluster is generally similar in all molecules examined, with dihedrals between the Ru(1,2,3) and Ru(1,2)C(1) planes ranging from 62.6(2) to 64.4(6)°, with the exception of **16** [55.0, 55.5(2)°], presumably as a result of the open edge of the Ru_3 cluster being Ru(2)···Ru(3). Angles between C(1)–C(2) and the Ru(1,2)C(1) plane range between 153.9(2) and 159(1)°. Comparisons of these structures with those of $Fe_3(\mu_3\text{-}CCCR_2)(\mu\text{-}CO)(CO)_9$ (RR′ = Me_2,[15] HPh,[16] Ph_2[17]) and with $Os_3(\mu\text{-}H)(\mu_3\text{-}CCCPh_2)(\mu\text{-}OH)(CO)_9$[3] confirm the structural rigidity of the allenylidene ligand commented upon earlier, with angles at C(2) of 148.8(8), 153.8(4) and 151.5(2)° (for the Fe complexes) and 145(3)° (for the Os complex). The coordinated and non-coordinated C(2)–C(3) separations are also similar to those found in the present study.

In organic allenes $R_2C{=}C{=}CR_2$, the C_3 chain is linear and the dihedral angle between the two CR_2 planes is 90°. Coordination of the allenylidene ligand to the cluster results in a bending of the C_3 chain [values found here range between 144(2) and 154.0(5)°]. Within the limits of precision, angle sums at C(3) are

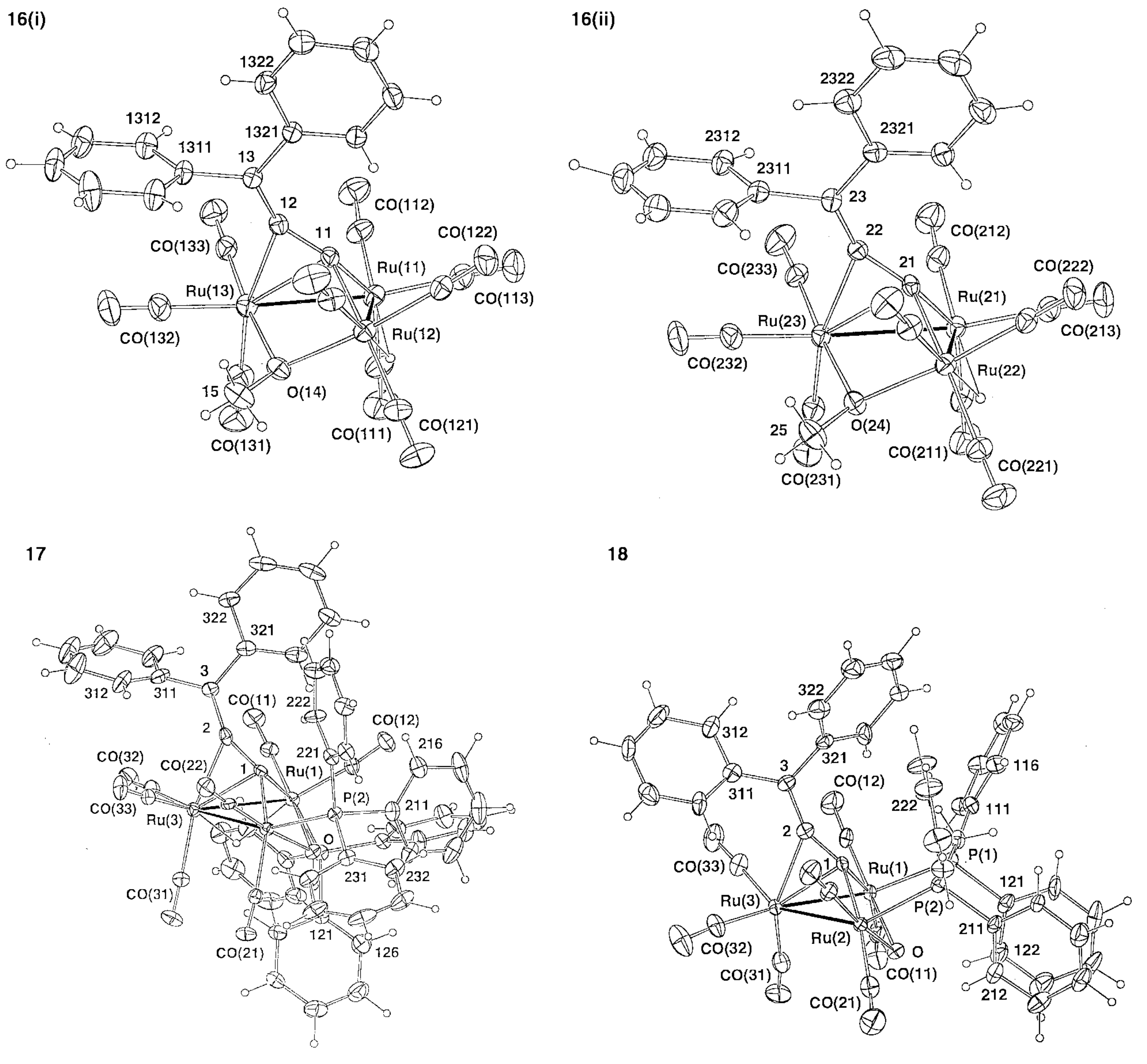


Fig. 1 Projections of **16** (two molecules)–**18**, with similar orientation and labelling, oblique to their Ru_3 planes. 20% thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

360°. Dihedral angles between C(3)C(31,32) and Ru(1,2)C(1) show considerable differences, ranging between 48.7(5) (for **22**) and 81.0(2)° (for **16**), with no correlation with the angle at C(3).

In **17**, one PPh_3 ligand occupies an axial position on Ru(1), whereas the PPh_3 ligand on Ru(2) is in an equatorial coordination site. This is presumably because of the necessity to minimise steric interaction between the phenyl groups of the two ligands, and results in P(1) and P(2) being approximately *trans* and *cis*, respectively, to C(1) [P(1)–Ru(1)–C(1) 163.7(3), P(2)–Ru(2)–C(1) 107.2(3)°]. In contrast, both P atoms in **18** are in equatorial sites [P(1)–Ru(1)–C(1) 92.3(4), P(2)–Ru(2)–C(1) 87.8(4)°]. In the dppm ligands of **18**, **20** and **21**, lengthening of the Ru(1)–Ru(2) vector, accompanied by diminished Ru–P distances, appears to have no significant effect on the internal angles at P(1,2) and C(0), differences in these values in analogous complexes **20** and **21** being greater than those with **18**.

In the $AuRu_3$ cluster **22**, the Au–Ru separations are 2.708(1) and 2.754(2) Å, with an interplanar angle Ru(1,2,3) / AuRu(1,2) of 65.70(4)°. These dimensions are similar to those found in other complexes of this type. In conformity with the isolobal concept, in this example the $Au(PPh_3)$ group occupies the same position as one of the H atoms in **19**.

In **13**, the four independent molecules make up the asymmetric unit, molecule 2 being depicted in Fig. 3 as representative while Table 3 contains the important bond parameters. This complex is a typical example of a hydrido–alkynyl complex, with the latter group sited perpendicularly to the Ru(1)–Ru(2) vector. However, the crystal appears to show evidence of disorder with expected consequences for the precision of the determination; ligand light atom components corresponding to minor disordered moieties are not resolved, so that their relationship to the Ru_3 clusters is not apparent. The most notable difference between the four independent molecules of the asymmetric unit is the disposition of the $CH_2(OH)(n\#)$ group, the oxygen atom variously disposed relative to the $Ru(n\#)$-$CO(n33)C(n1,n2,n3)$ plane, with unduly large amplitudes possibly a foil for disorder. This is most clearly suggested in molecule 4 where the associated geometry of an in-plane substituent is clearly unrealistic.

Discussion

Attempts to make ruthenium and osmium cluster complexes containing propargyl alcohols were first reported in 1982, when the parent cluster carbonyls $M_3(CO)_{12}$ (M = Ru, Os) were heated with the alcohols in refluxing octane.[3] For ruthenium, only small amounts of the expected $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2CPh_2\text{-}(OH)\}(CO)_9$ were obtained, although the analogous osmium compound was isolated in good yield. Use of the activated ruthenium cluster $Ru_3(CO)_{10}(NCMe)_2$ has enabled us to

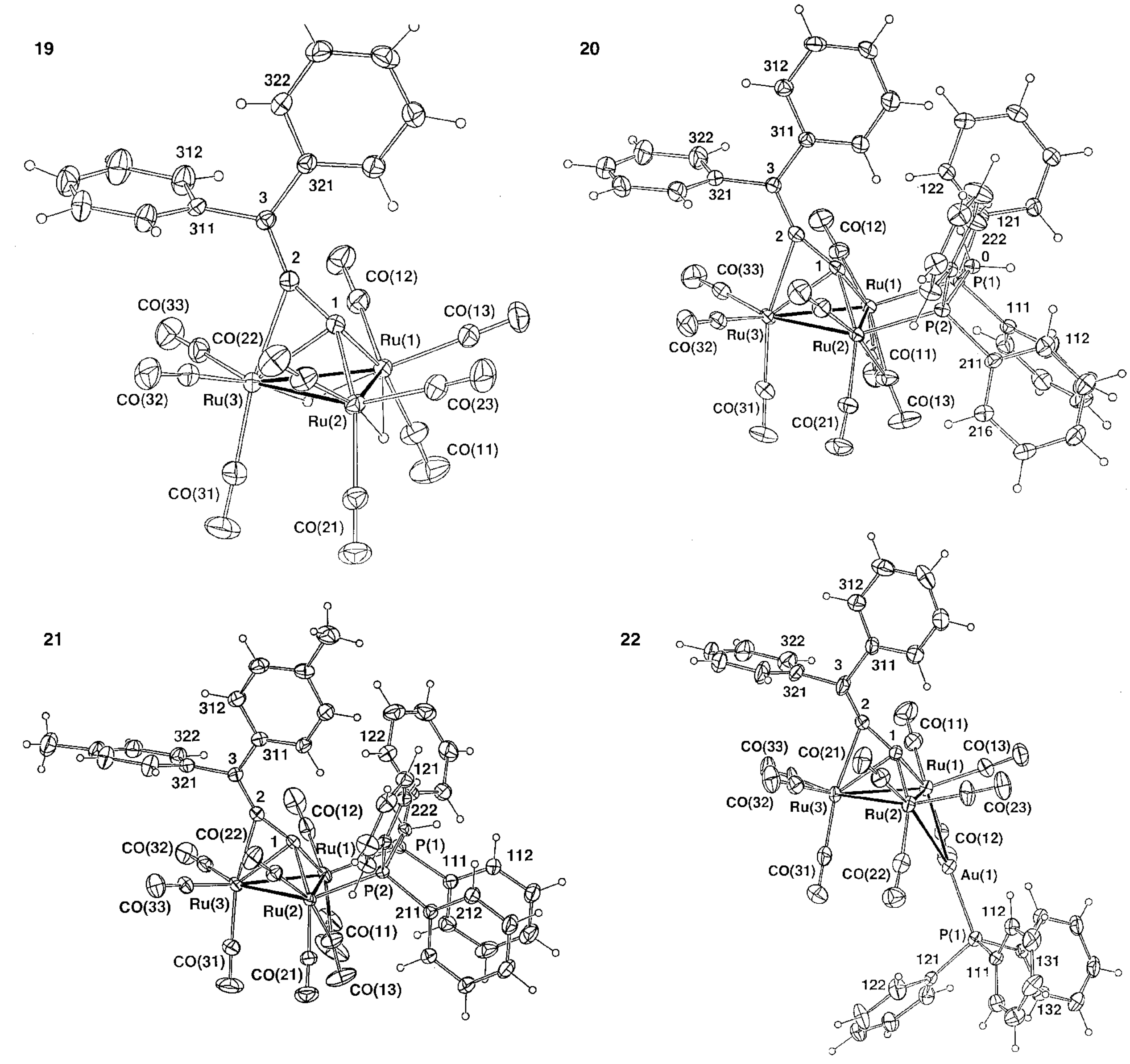


Fig. 2 Projections of **19**–**22**, see notes for Fig. 1.

improve significantly the yields of complexes of this type and to examine further their reactions. In this way, we have isolated $Ru_3\{\mu_3\text{-}HC_2CR_2(OH)\}(\mu\text{-}CO)(CO)_9$ (R = H, Me, Ph) from reactions carried out at ambient temperatures in yields of between 39 and 74%. These complexes resemble the many other similar derivatives that have been obtained from other alkynes, as shown by their spectral properties.

As commonly found with 1-alkyne derivatives, ready conversion of these complexes into the hydrido–alkynyl clusters occurs in refluxing hexane in yields of 71 to 89%, some of these derivatives being isolated from the initial reactions involving the alkyne, *e.g.* for R = Me. One example has been characterised crystallographically, albeit with limited precision. These cluster complexes retain the hydroxyl group on the alkynyl substituent. As found previously with the osmium cluster,[3] treatment with strong acid (aqueous CF_3CO_2H or HBF_4) results in migration of the hydroxy group from the alkynyl ligand to the cluster framework, with concomitant generation of an allenylidene ligand and opening of the M_3 cluster, the hydroxyl group bridging the non-bonded Ru···Ru vector. While for R = Ph, the product is obtained in 32% yield, use of $HBF_4{\cdot}OMe_2$ allowed essentially quantitative conversion and isolation of $Ru_3(\mu\text{-}H)(\mu_3\text{-}CCCPh_2)(\mu\text{-}OH)(CO)_9$ in 79% yield, together with 7% of the analogous μ-OMe derivative **16**, apparently formed from the dimethyl ether. The hydroxy cluster **15** reacts with tertiary phosphines to substitute one CO group on each of the terminal ruthenium atoms of the open Ru_3 cluster. In the case of **18**, the bidentate ligand bridges the non-bonded Ru···Ru vector, together with the OH group.

For a study of these allenylidene clusters, it was desirable that other functional groups, such as OH, were not present. Consequently, we have been interested to establish a method of generating the allenylidene ligand by reactions in which the OH group is eliminated, rather than transferred to the cluster. The reactions we have described herein give some insight as to how this might be achieved.

Protonation of the hydroxy–alkynyl clusters is likely to occur at the alkynyl OH group to give an oxonium ion. Elimination of either H_3O^+ (formed by combination with the cluster hydride) or H_2O would give the neutral allenylidene or protonated carbocationic cluster, respectively.[3] Either is an unsaturated 46-e system (**A**) which would be expected to react with other ligands if present. The formation of the products from reactions of **15** or **16** carried out in the presence of $HBF_4{\cdot}OMe_2$ can be understood in the following terms.

In the absence of added ligand, oxidative addition of water or Me_2O to **A** gives the μ-OH (**15**) or μ-OMe (**16**) complexes. The (H + OR) combination gives an electron-rich 50-e species with Ru–Ru bond cleavage occurring concomitantly to give the observed open triangular clusters. The same products are

Table 2 Significant structural parameters for **16**–**22**. Bond lengths (Å) and bond angles (°)

	16	**17**	**18**
(a) Complexes **16**–**18**			
Ru(1)–Ru(2)	2.8418(7), 2.8501(7)	3.234(1)	3.194(2)
Ru(1)–Ru(3)	2.8266(7), 2.8340(6)	2.920(1)	2.805(2)
Ru(2)–Ru(3)	3.3171(7), 3.3198(7)	2.810(1)	2.904(2)
Ru(1)–P(1)		2.419(3)	2.317(4)
Ru(2)–P(2)		2.324(3)	2.328(4)
Ru(1)–O[a]		2.117(6)	2.135(9)
Ru(2)–O[a]	2.100(4), 2.096(4)	2.136(6)	2.11(1)
Ru(3)–O[a]	2.111(4), 2.110(4)		
Ru(1)–C(1)	2.010(5), 2.002(5)	2.10(1)	2.07(1)
Ru(2)–C(1)	2.097(5), 2.095(5)	2.054(9)	2.09(1)
Ru(3)–C(1)	2.248(6), 2.262(5)	2.20(1)	2.16(1)
Ru(3)–C(2)	2.223(5), 2.238(5)	2.24(1)	2.28(1)
P(1)–C(0)			1.84(2)
P(2)–C(0)			1.84(2)
C(1)–C(2)	1.349(6), 1.346(6)	1.35(2)	1.32(2)
C(2)–C(3)	1.337(7), 1.341(7)	1.37(2)	1.37(2)
C(3)–C(311)	1.490(7), 1.499(7)	1.50(2)	1.48(2)
C(3)–C(321)	1.483(8), 1.491(8)	1.48(2)	1.49(2)
Ru(2)–Ru(1)–Ru(3)	71.63(2), 71.47(2)	54.05(3)	57.48(4)
Ru(1)–Ru(3)–Ru(2)		68.68(3)	68.01(4)
Ru(1)–O(1)–Ru(2)		99.0(3)	97.5(2)
Ru(2)–O(4)–Ru(3)	103.9(2), 104.3(2)		
Ru(1)–P(1)–C(0)			110.7(5)
Ru(2)–P(2)–C(0)			113.7(5)
P(1)–C(0)–P(2)			118.4(8)
Ru(1)–C(1)–Ru(2)	87.5(2), 88.1(2)	102.2(5)	100.3(6)
Ru(1)–C(1)–C(2)	142.2(4), 142.3(4)	114.6(7)	132(1)
Ru(2)–C(1)–C(2)	123.1(4), 122.5(4)	133.7(8)	122(1)
C(1)–C(2)–C(3)	148.7(6), 148.8(5)	153(1)	153(1)
C(2)–C(3)–C(311)	121.7(5), 120.9(5)	122(1)	123(1)
C(2)–C(3)–C(321)	120.4(5), 120.5(4)	119(1)	119(1)
ΣC(3)	359.$_9$, 360.$_0$	360	360
Ru(1,2,3)/Ru(1,2)C(1)	55.0, 55.5(2)	64.4(6)	64.4(6)
Ru(1,2-mid-point)C(1)/C(1,2)	157, 157	159	159
ORu$_2$/Ru$_3$	44.4(2), 45.9(2)	47.7(3)	54.7(4)
Ru(1,2)C(1)/C(3,31,32)	81.0(2), 81.0(2)	63.3(4)	61.6(5)

	19	**20**	**21**	**22**
(b) Complexes **19**–**22**				
Au(1)–Ru(1)				2.708(1)
Au(1)–Ru(2)				2.754(2)
Ru(1)–Ru(2)	2.847(1)	2.7863(6)	2.7728(4)	2.891(1)
Ru(1)–Ru(3)	2.8747(9)	2.7733(5)	2.7519(5)	2.887(1)
Ru(2)–Ru(3)	2.7389(9)	2.7610(6)	2.8049(4)	2.779(2)
Au(1)–P(1)				2.291(3)
Ru(1)–P(1)		2.361(1)	2.3472(9)	
Ru(2)–P(2)		2.349(1)	2.3615(9)	
Ru(1)–C(1)	2.079(5)	2.071(5)	2.043(4)	2.07(1)
Ru(2)–C(1)	2.020(5)	2.026(5)	2.057(3)	2.02(1)
Ru(3)–C(1)	2.197(5)	2.181(4)	2.178(3)	2.21(1)
Ru(3)–C(2)	2.281(5)	2.259(5)	2.258(3)	2.29(1)
Ru(1)–C(13)		2.084(6)	2.195(5)	1.89(1)
Ru(2)–C(13)		2.209(6)	2.051(5)	
P(1)–C(0)		1.842(5)	1.846(4)	
P(2)–C(0)		1.847(5)	1.840(4)	
C(1)–C(2)	1.328(6)	1.339(6)	1.338(5)	1.35(2)
C(2)–C(3)	1.332(7)	1.357(6)	1.352(5)	1.31(2)
C(3)–C(311)	1.501(6)	1.479(6)	1.486(5)	1.51(2)
C(3)–C(321)	1.473(7)	1.498(7)	1.504(5)	1.52(2)
Ru(2)–Ru(1)–Ru(3)	58.22(2)	59.55(1)	61.02(1)	
Ru(1)–Ru(3)–Ru(2)	60.39(3)	60.46(1)	59.86(1)	
Ru(1)–P(1)–C(0)		110.2(1)	108.9(1)	
Ru(2)–P(2)–C(0)		109.3(1)	111.0(1)	
P(1)–C(0)–P(2)		119.3(2)	114.1(2)	
Ru(1)–C(1)–Ru(2)	88.0(2)	85.7(2)	85.1(1)	90.0(5)
Ru(1)–C(13)–Ru(2)		80.9(2)	81.4(2)	
Ru(1)–C(13)–O(13)		141.4(5)	134.1(4)	
Ru(2)–C(13)–O(13)		137.7(5)	144.3(4)	
Ru(1)–C(1)–C(2)	124.3(4)	128.1(4)	132.2(3)	124(1)
Ru(2)–C(1)–C(2)	138.4(4)	134.5(4)	131.6(3)	137(1)
C(1)–C(2)–C(3)	153.4(5)	154.0(5)	153.0(3)	144(2)
C(2)–C(3)–C(311)	120.7(5)	119.9(4)	121.1(3)	121(1)
C(2)–C(3)–C(321)	121.3(4)	119.3(4)	120.1(3)	119(1)
ΣC(3)	359.$_9$	359.$_9$	359.$_9$	355
Ru(1,2,3)/Ru(1,2)C(1)	62.6(2)	63.4(2)	62.7(1)	63.4(5)
Ru(1,2-mid-point)C(1)/C(1,2)	155	154	155	155
O(Au)Ru$_2$/Ru$_3$		66.7(2)		65.70(4)
Ru(1,2)C(1)/C(3,31,32)	50.1(2)	67.7(1)	50.0(1)	48.7(5)

[a] O to be read as O(*n*) (*n* = 1 or 4) as appropriate.

Table 3 Some structural parameters for **13**. Bond distances (Å) and bond angles (°) (major component only)

	Molecule 1	Molecule 2	Molecule 3	Molecule 4	Average
Ru(1)–Ru(2)	2.768(2)	2.782(2)	2.783(2)	2.782(2)	2.779(7)
Ru(1)–Ru(3)	2.810(2)	2.807(2)	2.807(3)	2.793(3)	2.806(5)
Ru(2)–Ru(3)	2.810(2)	2.813(2)	2.815(2)	2.792(2)	
Ru(1)–C(1)	2.22(2)	2.21(1)	2.25(2)	2.25(3)	2.21(1)
Ru(2)–C(1)	2.24(2)	2.17(2)	2.17(2)	2.16(2)	
Ru(1)–C(2)	2.22(2)	2.26(2)	2.22(2)	2.48(2)	2.23(2)[a]
Ru(2)–C(2)	2.24(2)	2.25(2)	2.21(2)	2.48(1)	1.89(1)
Ru(3)–C(1)	1.91(2)	1.88(2)	1.90(2)	1.88(2)	
C(1)–C(2)	1.33(2)	1.37(2)	1.33(3)	1.09(3)	1.34(2)[a]
C(2)–C(3)	1.52(3)	1.49(3)	1.52(2)	1.64(3)	1.51(1)[a]
C(3)–O	1.26(3)	1.35(2)	1.40(2)	1.27(4)	1.32(7)
Ru(3)–C(1)–C(2)	151(2)	156(1)	152(1)	173(2)	153(3)[a]
C(1)–C(2)–C(3)	141(2)	144(2)	142(2)	170(1)	142(1)[a]
C(2)–C(3)–O	114(2)	117(2)	111(1)	135(2)	114(2)[a]

[a] Omitting the values for molecule 4.

obtained in the presence of CO, rather than the sought-after Ru(μ_3-CCCPh$_2$)(μ-CO)(CO)$_9$, probably because of the very limited solubility of CO in the reaction medium.

Reactions of dppm with **9** or **10**, carried out in the presence of one equivalent of $HBF_4 \cdot OMe_2$, also result in loss of the elements of water (OH + H) with formation of **20** and **21**, respectively. The formation of these products can be understood if the unsaturated intermediate **A** reacts quickly with the

13

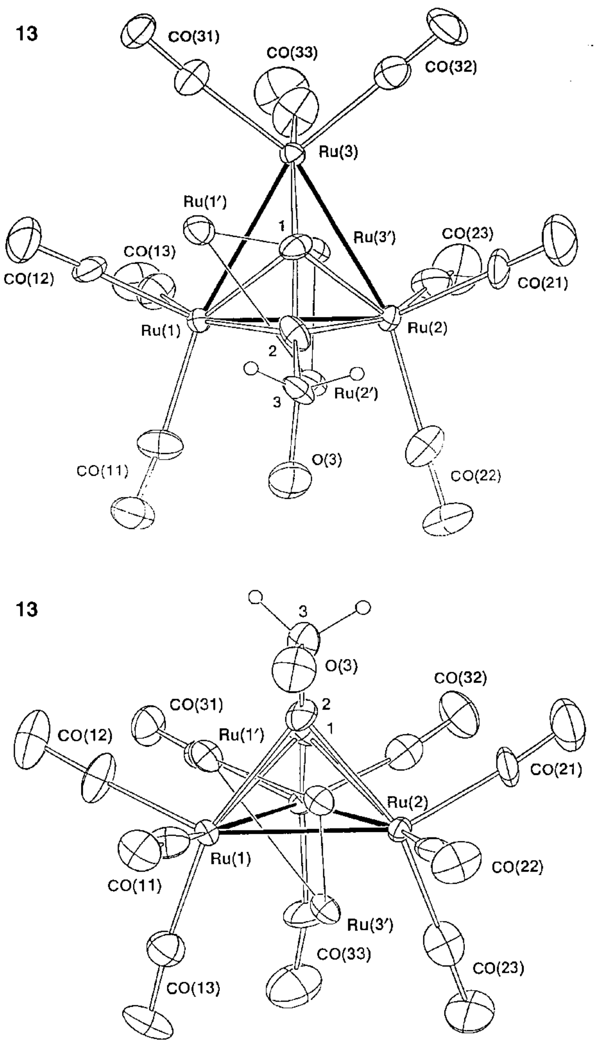


Fig. 3 Projection of molecule 2 as representative of **13**, normal and oblique to the principal Ru_3 plane. Primed ruthenium atoms are minor disordered components, associated ligand components not being resolved.

diphosphine; a molecule of CO is also lost to give the obseved products. Elsewhere, we have described the unusual transformation of the allenylidene ligand into a diphenylindenyl group by combination with one of the phenyl groups of the dppm ligand, which occurs on heating.[13a]

Treatment of **9** with $K[BHBu^s_3]$, followed by protonation, resulted in loss of water and afforded a small amount of $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}CCCPh_2)(CO)_9$ (**19**). This complex has limited stability in air and in solution, considerable decomposition occurring during its preparation, with much of the ruthenium being recovered as tetranuclear cluster hydrido–carbonyls. This product may arise by loss of water after protonation, followed by addition of H_2 (present in limited amount in soluton from the reaction of $K[BHBu^s_3]$ with acid) or of H^+/H^- to the intermediate **A**. On the other hand, treatment of the hydroxy–allenylidene cluster **15** with $K[BHBu^s_3]$, followed by AuCl-(PPh_3), results in loss of OH and auration of the cluster. The resulting complex **22** is isolobal with **19**, and may also result from reaction of **A** with $[Au(PPh_3)]^+$ present in the solution.

Conclusions

The work described above has clarified the chemistry of the Ru_3 cluster with propargyl alcohols and their conversion into allenylidene complexes. While the elimination of water is not spontaneous with these complexes, in contrast to their mononuclear counterparts, conditions for the preparation of several clusters containing allenylidene but no hydroxy groups have been established. Further accounts of the chemistry of these interesting complexes are in preparation.

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. Elemental analyses were performed by Canadian Microanalytical Service, Delta, B.C., Canada. Preparative tlc was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thick).

Instrumentation

IR: Perkin-Elmer 1720X FT IR. NMR: Bruker CXP300 or ACP300 (^1H NMR at 300.13 MHz, ^{13}C NMR at 75.47 MHz) or Varian Gemini 200 (^1H at 199.8 MHz, ^{13}C at 50.29 MHz) spectrometers. Samples were dissolved in $CDCl_3$ (Sigma) or $(CD_3)_2SO$ (Aldrich) and spectra were recorded using 5 mm sample tubes. ES MS: VG Platform II: Solutions in MeOH were injected *via* a 10 ml injection loop; nitrogen was used as the drying and nebulising gas. Samples were examined at cone voltages in the range 20–80 V to find the best conditions. Finnegan LCQ: Solutions were directly infused into this instrument. Chemical aids to ionisation were used as required.[17]

Reagents

$HC{\equiv}CCR_2(OH)$ [R = H, Me (Aldrich), Ph,[18] tol[18]], $Ru_3(CO)_{10}(NCMe)_2$,[19] $HBF_4{\cdot}OMe_2$, PPh_3, dppm, $AuCl(PPh_3)$[20] and $K[BHBu^s_3]$ (Aldrich; K-Selectride) either were prepared according to the cited methods or were commercial products, used as received.

Synthesis of $Ru_3\{\mu_3\text{-}HC_2CPh_2(OH)\}(\mu\text{-}CO)(CO)_9$ (7). A solution of $HC{\equiv}CCPh_2(OH)$ (70 mg, 0.312 mmol) was added to one of $Ru_3(CO)_{10}(NCMe)_2$ [from $Ru_3(CO)_{12}$ (200 mg, 0.312 mmol) prepared as above]. After 1 h at rt, the colour of the mixture had darkened to orange. Preparative tlc (silica gel, benzene–hexane 1 : 1) gave $Ru_3(CO)_{12}$ (11 mg, 5.4%) and $Ru_3\{\mu_3\text{-}HC_2CPh_2(OH)\}(\mu\text{-}CO)(CO)_9$ (**7**) (182 mg, 74%), in the major orange band (R_f 0.40) and obtained as orange crystals from pentane.

Synthesis of $Ru_3\{\mu_3\text{-}HC_2C(tol)_2(OH)\}(\mu\text{-}CO)(CO)_9$ (8). A solution of $HC{\equiv}CC(tol)_2(OH)$ (74 mg, 0.312 mmol) in CH_2Cl_2 (2 ml) was added to $Ru_3(CO)_{10}(NCMe)$ [prepared from $Ru_3(CO)_{12}$ (200 mg, 0.312 mmol) and Me_3NO (60 mg, 0.8 mmol) in a mixture of CH_2Cl_2 (80 ml) and MeCN (20 ml) at 0 °C]. The mixture was allowed to warm up to rt and left for 2 h, after which it had become orange. Evaporation to dryness and purification of the residue by preparative tlc (acetone–hexane 1 : 4) gave an orange band (R_f 0.39) which contained $Ru_3\{\mu_3\text{-}HC_2C(tol)_2(OH)\}(\mu\text{-}CO)(CO)_9$ (**8**) (202 mg, 79%), obtained as an orange solid.

Synthesis of $Ru_3\{\mu_3\text{-}HC_2CH_2(OH)\}(\mu\text{-}CO)(CO)_9$ (11). Propargyl alcohol (17 mg, 0.018 mmol) was added to $Ru_3(CO)_{10}(NCMe)_2$ [prepared as above from $Ru_3(CO)_{12}$ (200 mg, 0.312 mmol)] at −50 °C. After warming to rt and stirring for 30 min, the colour of the mixture was dark orange. Preparative tlc (silica gel, acetone–hexane 1 : 4) separated the major product as an orange band (R_f 0.5) which gave orange crystals of $Ru_3\{\mu_3\text{-}HC_2CH_2(OH)\}(\mu\text{-}CO)(CO)_9$ (**11**) (78 mg, 39%). Two minor yellow products were not identified; some decomposition products were left on the baseline.

Synthesis of $Ru_3\{\mu_3\text{-}HC_2CMe_2(OH)\}(\mu\text{-}CO)(CO)_9$ (12). A solution of $HC{\equiv}CCMe_2(OH)$ (66 mg, 0.196 mmol) in CH_2Cl_2 (2 ml) was added to a solution of $Ru_3(CO)_{10}(NCMe)_2$ [prepared as above from $Ru_3(CO)_{12}$ (250 mg, 0.39 mmol)] at −50 °C. After warming to rt and stirrring for 45 min, the colour of the mixture had changed from pale yellow to orange. Solvents were removed under vacuum and the residue was purified by preparative tlc (silca gel, acetone–hexane 1 : 4). The fastest-moving band contained $Ru_3(CO)_{12}$ (<1%). The second band (yellow, R_f 0.48) contained $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2CMe_2(OH)\}(CO)_9$ (**14**) (27.4 mg, 11%), obtained as yellow crystals (CH_2Cl_2–MeOH). Band 3 (orange, R_f 0.38) afforded $Ru_3\{\mu_3\text{-}HC_2CMe_2(OH)\}(\mu\text{-}CO)(CO)_9$ (**12**) (140 mg, 54%) as orange crystals (CH_2Cl_2–MeOH).

Preparation of $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2CPh_2(OH)\}(CO)_9$ (9). A solution of $Ru_3\{\mu_3\text{-}HC_2CPh_2(OH)\}(\mu\text{-}CO)(CO)_9$ (**7**) (130 mg, 0.164 mmol) in hexane (20 ml) was heated at reflux point for 1 h, after which the colour had paled to yellow. Purification by preparative tlc (acetone–hexane 3 : 7) gave pale yellow crystals (pentane) of $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2CPh_2(OH)\}(CO)_9$ (**9**) (108 mg, 86%) obtained from the band with R_f 0.54.

Preparation of $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2C(tol)_2(OH)\}(CO)_9$ (10). A solution of $Ru_3\{\mu_3\text{-}HC_2C(tol)_2(OH)\}(\mu\text{-}CO)(CO)_9$ (**8**) (450 mg, 0.55 mmol) in hexane (50 ml) was heated at reflux point for 1 h, the colour gradually changing to yellow. Preparative tlc (acetone–hexane 1 : 4) gave a single yellow band (R_f 0.66), which after extraction and crystallisation (pentane) afforded pale yellow crystals of $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2C(tol)_2(OH)\}(CO)_9$ (**10**) (383 mg, 88%).

Preparation of $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2CH_2(OH)\}(CO)_9$ (13). A solution of $Ru_3\{\mu_3\text{-}HC_2CH_2(OH)\}(\mu\text{-}CO)(CO)_9$ (**11**) (100 mg, 0.156 mmol) in hexane (20 ml) was heated at reflux point for 15 min, after which time tlc showed complete disappearance of starting material. Purification by preparative tlc (silica gel, acetone–hexane 1 : 4) gave yellow crystals ($CHCl_3$) of $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2CH_2(OH)\}(CO)_9$ (**13**) (68 mg, 71%).

Preparation of $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2CMe_2(OH)\}(CO)_9$ (14). A solution of $Ru_3\{\mu_3\text{-}HC_2CMe_2(OH)\}(\mu\text{-}CO)(CO)_9$ (**12**) (84 mg, 0.126 mmol) in hexane (15 ml) was heated at reflux point for 15 min, after which time the colour had changed from orange to pale yellow. Purification by preparative tlc (silica gel, acetone–hexane 1 : 4) gave yellow $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2CMe_2(OH)\}(CO)_9$ (**14**) (72 mg, 90%).

Reaction of $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2CPh_2(OH)\}(CO)_9$ with $HBF_4\cdot Me_2O$. Six drops of $HBF_4\cdot Me_2O$ were added to a solution of $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2CPh_2(OH)\}(CO)_9$ (60 mg, 0.079 mmol) in CH_2Cl_2 (7 ml), whereupon the colour changed immediately from pale yellow through dark red to red-orange. After stirring at rt for 15 min, tlc showed that two new complexes were present. Separation by preparative tlc (silica gel, acetone–hexane 3 : 7) gave two yellow bands. The first (R_f 0.063) contained $Ru_3(\mu\text{-}H)(\mu_3\text{-}CCCPh_2)(\mu\text{-}OMe)(CO)_9$ (**16**) (4.2 mg, 7%) as yellow crystals (hexane). The second band (R_f 0.56) gave $Ru_3(\mu\text{-}H)(\mu_3\text{-}CCCPh_2)(\mu\text{-}OH)(CO)_9$ (**15**) (47.5 mg, 79%) as a yellow powder.

Reactions of $Ru_3(\mu\text{-}H)(\mu_3\text{-}CCCPh_2)(\mu\text{-}OH)(CO)_9$ (15) with tertiary phosphines. *(a) PPh_3.* A mixture of $Ru_3(\mu\text{-}H)(\mu_3\text{-}CCCPh_2)(\mu\text{-}OH)(CO)_9$ (60 mg, 0.08 mmol) and PPh_3 (42 mg, 0.16 mmol) was heated in refluxing toluene (10 ml) for 15 min. After evaporation of solvent, the residue was separated by preparative tlc (silica gel, acetone–hexane 3 : 7) to give a major yellow band (R_f 0.37) which afforded yellow-orange crystals of $Ru_3(\mu\text{-}H)(\mu_3\text{-}CCCPh_2)(\mu\text{-}OH)(CO)_7(PPh_3)_2$ (**17**) (26.2 mg, 27%) from $CHCl_3$–MeOH.

(b) dppm. A similar reaction between $Ru_3(\mu\text{-}H)(\mu_3\text{-}CCCPh_2)(\mu\text{-}OH)(CO)_9$ (75 mg, 0.10 mmol) and dppm (38 mg, 0.10 mmol) afforded orange crystals of $Ru_3(\mu\text{-}H)(\mu_3\text{-}CCCPh_2)(\mu\text{-}OH)(\mu\text{-}dppm)(CO)_7$ (**18**) (60 mg, 56%) from CH_2Cl_2–MeOH.

Reaction of $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2CPh_2(OH)\}(CO)_9$ with $K[BHBu^s{}_3]$ and $HBF_4\cdot Me_2O$. K-Selectride (1M in thf, 0.35 ml) was added to $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2CPh_2(OH)\}(CO)_9$ (250 mg, 0.32 mmol) in thf (7 ml). After stirring for 5 min at rt, the mixture was treated with $HBF_4\cdot OMe_2$ (0.05 ml) and stirred for a further 30 min. Evaporation and separation by preparative tlc (hexane) gave several bands. The first yellow band (R_f 0.49) contained $Ru_4(\mu\text{-}H)_4(CO)_{12}$ (9.1 mg, 4%), identified from its IR ν(CO) and ^1H NMR spectra. An orange band (R_f 0.33) contained $Ru_4(\mu\text{-}H)_2(CO)_{13}$ (11 mg, 6%), identified from its IR ν(CO) and ^1H NMR spectra and by an X-ray structure determination. The second yellow band (R_f 0.26) afforded $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}CCCPh_2)(CO)_9$ (**19**) (4.6 mg, 2%) as yellow crystals (pentane).

Preparation of $Ru_3(\mu_3\text{-}CCCPh_2)(\mu\text{-}dppm)(\mu\text{-}CO)(CO)_7$ (20). A few drops of $HBF_4\cdot OMe_2$ were added to a solution of $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2CPh_2(OH)\}(CO)_9$ (60 mg, 0.078 mmol) and dppm (30 mg, 0.078 mmol) in CH_2Cl_2 (10 ml) at rt. The colour immediately changed to dark red. After 30 min, tlc showed that reaction was complete. After removal of solvent, the residue was recrystallised (CH_2Cl_2–MeOH) to give dark red crystals of $Ru_3(\mu_3\text{-}CCCPh_2)(\mu\text{-}dppm)(\mu\text{-}CO)(CO)_7$ (**20**) (58 mg, 67%).

Preparation of $Ru_3\{\mu_3\text{-}CCC(tol)_2\}(\mu\text{-}dppm)(\mu\text{-}CO)(CO)_7$ (21). This complex was prepared from $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2C(tol)_2(OH)\}(CO)_9$ (460 mg, 0.58 mmol), dppm (220 mg, 0.58 mmol) and a few drops of $HBF_4\cdot OMe_2$ in a similar manner to **20** above. Separation by preparative tlc gave dark red crystals (CH_2Cl_2–hexane) of $Ru_3\{\mu_3\text{-}CCC(tol)_2\}(\mu\text{-}dppm)(\mu\text{-}CO)(CO)_7$ (**21**) (506 mg, 77%).

Auration of $Ru_3(\mu\text{-}H)(\mu_3\text{-}CCCPh_2)(\mu\text{-}OH)(CO)_9$ (15). A solution of $Ru_3(\mu\text{-}H)(\mu_3\text{-}CCCPh_2)(\mu\text{-}OH)(CO)_9$ (50 mg, 0.07 mmol) in thf (7 ml) was treated with K-Selectride (0.2 ml of a 1M solution in thf). After stirring at rt for 15 min, $AuCl(PPh_3)$ (35 mg, 0.07 mmol) was added to the mixture, which was stirred for a further 30 min. Separation of the product by preparative tlc (silica gel, acetone–hexane 1 : 4) gave yellow crystals of $AuRu_3(\mu\text{-}H)(\mu_3\text{-}CCCPh_2)(CO)_9(PPh_3)$ (**22**) (16.5 mg, 21%) from the band with R_f 0.47. Several other products are formed, but in amounts too small to isolate and characterise satisfactorily.

Structure determinations

For **17**–**19** and **22**, unique single-counter/four-circle diffractometer data sets were measured at *ca.* 295 K within the specified $2\theta_{max}$ limit, yielding N independent reflections, N_o with $I > 3\sigma(I)$ being used in the full matrix least squares refinements after gaussian absorption correction. For the remainder, full spheres of data were measured using a Bruker AXS CCD instrument at *ca.* 300 K, N_{tot} reflections being merged after 'empirical' absorption correction (proprietary software SMART, SAINT, SADABS[22]) to N unique (R_{int} quoted), N_o with $F > 4\sigma(F)$ being used in the refinement. All data were measured using monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å. In the refinements, anisotropic thermal parameter forms were used for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimated values. Conventional residuals R, R_w on $|F|$ are quoted, statistical weights being employed. Neutral atom complex scattering factors were used; computation used the XTAL 3.4 program system.[21] Pertinent results are given in the Figures (which show non-hydrogen atoms with 20% probability amplitude displacement ellipsoids) and Tables. See Table 4 for crystal and refinement data.

Individual variations associated with particular structures follow: **13**. Four distinct molecules comprise the asymmetric unit of the structure. As is not uncommon, the Ru_3 triangles were found to be disordered, site occupancies refining to 0.861(2), 0.774(2), 0.825(2) and 0.718(2), and complements for the disordered component. The mode of disorder is unusual, however, the sites not conforming to the usual 'Star of David'

Table 4 Crystal and refinement data

Compound	**13**	**16**	**17**	**18**	**19**	**20**	**21**	**22**
Formula	$C_{12}H_4O_{10}Ru_3$	$C_{25}H_{14}O_{10}Ru_3$	$C_{58}H_{42}O_8P_2$-Ru_3	$C_{47}H_{34}O_8P_2$-$Ru_3\cdot0.56CH_2$-Cl_2	$C_{24}H_{12}O_9Ru_3$	$C_{48}H_{32}O_8$-P_2Ru_3	$C_{50}H_{36}O_8P_2$-$Ru_3\cdot\approx0.64CH_2$-Cl_2	$C_{42}H_{25}AuO_9$-PRu_3
M	611.4	777.6	1232.1	1134.4	747.6	1101.9	1182.6	1204.8
Crystal system	Triclinic	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$Pca2_1$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a/Å	14.611(2)	19.279(2)	10.660(1)	20.743(6)	10.477(3)	10.3021(8)	13.078(2)	16.573(7)
b/Å	16.761(2)	18.672(2)	14.393(4)	11.600(5)	12.434(3)	10.0375(8)	24.641(3)	13.754(6)
c/Å	17.082(2)	7.7598(9)	34.288(11)	19.813(4)	20.465(9)	42.729(3)	15.348(2)	9.797(6)
α/°	88.463(2)	90.257(2)						99.18(4)
β/°	65.661(2)	97.639(2)	95.38(2)		105.19(3)	94.181(1)	96.585(2)	95.47(4)
γ/°	66.170(2)	99.825(2)						106.11(3)
V/Å^3	3437	2727	5237	4767	2573	4407	4913	2095
Z	8	4	4	4	4	4	4	2
D_c/g cm^{-3}	2.36_2	1.89_4	1.56_2	1.58_0	1.92_7	1.66_1	1.59_9	1.91_0
Crystal size/ mm	0.17 × 0.15 × 0.07	0.55 × 0.40 × 0.25	0.28 × 0.10 × 0.12	0.18 × 0.14 × 0.51	0.25 × 0.45 × 0.28	0.36 × 0.25 × 0.21	0.31 × 0.28 × 0.11	0.10 × 0.07 × 0.24
T (min, max)	0.71, 0.89	0.57, 0.89	0.91, 0.93	0.82, 0.86	0.60, 0.67	0.78, 0.89	0.65, 0.86	0.62, 0.76
μ/cm^{-1}	26.5	16.9	9.7	11.1	17.9	11.4	10.9	46.4
$2\theta_{max}$/°	58	58	50	55	55	58	58	50
N	40329	30524			12339	48061	53658	
N_r (R_{int})	12029 (0.039)	13318 (0.050)	9206	4972	5903 (0.041)	11111 (0.024)	12360 (0.035)	7359
N_o	7869	8703	5018	143	4060	9632	9458	4591
R	0.062	0.046	0.055	48	0.040	0.049	0.041	0.049
R_w	0.064	0.048	0.054	57	0.037	0.056	0.050	0.046

dispositions, coplanar with the parent, but subject to rotation and displacement *and* twisting in the third dimension; Ru(1–3)/Ru(1′–3′) interplanar dihedrals are 62.3(3), 60.6(2), 60.3(2) and 61.7(2)° for the four molecules. Molecule 2, shown in Fig. 1, is fairly typical. Not infrequently, such disorder is found to be temperature dependent; a separate experiment conducted with this material at 150 K, using a smaller specimen, showed no appreciable change in site occupancies and the more precise room temperature determination is offered as typical. Disordered components of the remainder of the molecule were not resolved, presumably encompassed by some rather large ellipsoid amplitudes and, in turn, accounting for the rather high residuals. Hydroxyl and hydrido hydrogen atoms were not located in difference maps. **16**. (x, y, z, U_{iso})$_H$ were refined throughout, excepting those associated with the methyl groups, which were constrained at estimated values; two molecules comprise the asymmetric unit of the structure. **17**. Hydride and hydroxyl hydrogen atoms were defined in difference maps but not refined. **18**. Residuals were the same for both hands. The hydroxyl hydrogen atom was not located. The N_o criterion was $I > 2\sigma(I)$. **19**. Data were measured for a hemisphere, R_{int} 0.041. (x, y, z, U_{iso})$_H$ were refined throughout. The N_o criterion was $I > 2\sigma(I)$.

CCDC reference number 186/1807.

See http://www.rsc.org/suppdata/dt/a9/a906379j/ for crystallographic files in .cif format.

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