DALTON
FULL PAPER

Acetylene incorporation into the spiked framework of the phosphinidene and arsinidene clusters $[Ru_4(CO)_{13}(\mu\text{-}H)_2(\mu_4\text{-}ECF_3)]$ (E = P or As): skeletal rearrangement and crystal structures of a series of tetranuclear ruthenium clusters bearing alkynes

How Ghee Ang,* Siau Gek Ang and Shaowu Du

Department of Chemistry, National University of Singapore, 119260, Singapore

Received 14th April 1999, Accepted 14th July 1999

Reactions of $[Ru_4(CO)_{13}(\mu\text{-}H)_2(\mu_4\text{-}ECF_3)]$ (E = P **1** or As **2**) with RC≡CR (R = Ph or H) under mild conditions yielded square planar clusters $[Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}ECF_3)(RC_2R)]$ (E = As, R = Ph **3**; E = P, R = Ph **4** or E = P, R = H **5**) in which the acetylene ligands are attached to the metal square planes *via* $2\sigma + 4\pi$ bonds. Under similar conditions, the reaction of **1** with $CF_3C{\equiv}CCF_3$ afforded a similar cluster $[Ru_4(CO)_{12}(\mu_4\text{-}PCF_3)(CF_3C_2CF_3)]$ **6** in which the acetylene interacts with the Ru_4 square face only by 4σ bonds. Reactions of **1** and **2** with MeC≡CMe resulted in metal skeletal rearrangement and P–C bond formation to form the butterfly cluster $[Ru_4(CO)_{10}(\mu\text{-}CO)_2\{CF_3PC(Me)C(Me)\}]$ **7** and alkyne dimerization at the spiked Ru atom to form spiked clusters $[Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}ECF_3)(C_4Me_4)]$ (E = P **8** or As **9**) containing a metallocyclic RuC_4Me_4 ring. Reaction of **1** with diphenylbutadiyne under similar conditions afforded a square planar cluster $[Ru_4(CO)_{11}(\mu_4\text{-}PCF_3)\{PhC(H)C(H)CCPh\}]$ **10** where the bridging hydrogen migrates to the diyne to form a 1,4-diphenylbut-3-en-1-yne fragment attached to the Ru_4 face.

Introduction

The metal skeletal stereochemistry for tetraruthenium carbonyl clusters containing bridging and capping Group 15 ligands has been shown to have a range of structures, namely butterfly, square planar, tetrahedral and spiked. Among these the butterfly clusters have been shown to be reactive with alkynes and diynes.[1] Thus, Carty and his co-workers[2] reported that the reaction of butterfly clusters $[Ru_4(CO)_{13}(\mu_3\text{-}PPh)]$ with diphenylacetylene affords butterfly cluster $[Ru_4(CO)_{10}(\mu\text{-}CO)_2\{P(Ph)C(Ph)C(Ph)\}]$ and square planar cluster $[Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}PPh)(PhC_2Ph)]$. Furthermore, it has been reported that treatment of butterfly hydride $[Ru_4(CO)_{12}(\mu\text{-}H)_2(\mu_3\text{-}PPh)]$ with diphenylbutadiyne affords several square planar clusters containing co-ordinated *trans*-diphenylbutatriene and *trans*-diphenylbut-3-en-1-yne ligands.[3] However, no report has been made on the reactivity of tetraruthenium carbonyl clusters containing arsine ligands with alkynes. Herein, we report the reactivity and versatility of two spiked Ru_4 clusters $[Ru_4(CO)_{13}(\mu\text{-}H)_2(\mu_4\text{-}ECF_3)]$ (E = P or As) towards alkynes and diphenylbutadiyne. We found that different kinds of products were isolated depending on the alkynes employed.

Results and discussion

Syntheses and characterization

Reactions of spiked clusters $[Ru_4(CO)_{13}(\mu\text{-}H)_2(\mu_4\text{-}ECF_3)]$ (E = P **1** or As **2**) with RC≡CR at 70 °C in *p*-xylene for 18 h afford compounds with the formula $[Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}ECF_3)(RC_2R)]$ (E = As, R = Ph **3**; E = P, R = Ph **4** or H **5**). The yield of the diphenylacetylene derivative is greater for E = P than for As, and attempts to prepare the corresponding arsenic analogues of **5** were unsuccessful. The formation of clusters **3**, **4** and **5** involves novel skeletal rearrangement from spiked to square planar configuration. Under similar conditions, reaction of **1** with $CF_3C{\equiv}CCF_3$ results in the same skeletal rearrangement but affords a different product $[Ru_4(CO)_{12}(\mu_4\text{-}PCF_3)(CF_3C_2CF_3)]$ **6**, as illustrated in Scheme 1. Its arsenic analogue could not be isolated, indicating again the poor reactivity of arsinidene clusters.

When MeC≡CMe reacts with compound **1** at 70 °C in *p*-xylene for 18 h, unlike the above Ru_4 square planar clusters, a butterfly cluster $[Ru_4(CO)_{10}(\mu\text{-}CO)_2\{CF_3PC(Me)C(Me)\}]$ **7** is obtained. The formation of **7**, as shown in Scheme 1, involves a metal skeletal transformation from spiked to butterfly configuration along with the formation of a P–C (acetylene) bond. Another product isolated from this reaction is a spiked cluster $[Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}PCF_3)(C_4Me_4)]$ **8**, wherein dimerization of MeC≡CMe takes place on the spiked Ru atom with the metal skeleton remaining unchanged. Cluster **9**, an arsenic analogue of **8**, can also be isolated from the analogous reaction of **2** with MeCCMe. Treament of **1** with diphenylbutadiyne at 70 °C in *p*-xylene for 18 h results in the structural transformation and the migration of hydrogen from the cluster to the diyne to form square planar cluster **10**.

The IR and NMR data of the new cluster derivatives we have isolated are listed in Table 1. The carbonyl stretching frequencies fall in the region 1818–2200 cm^{-1}. The absorptions located at lower frequencies (1854–1897 cm^{-1}) of clusters **3**, **4**, **5**, **7**, **8** and **9** are attributed to the presence of bridging CO groups, which is supported by X-ray structural studies.

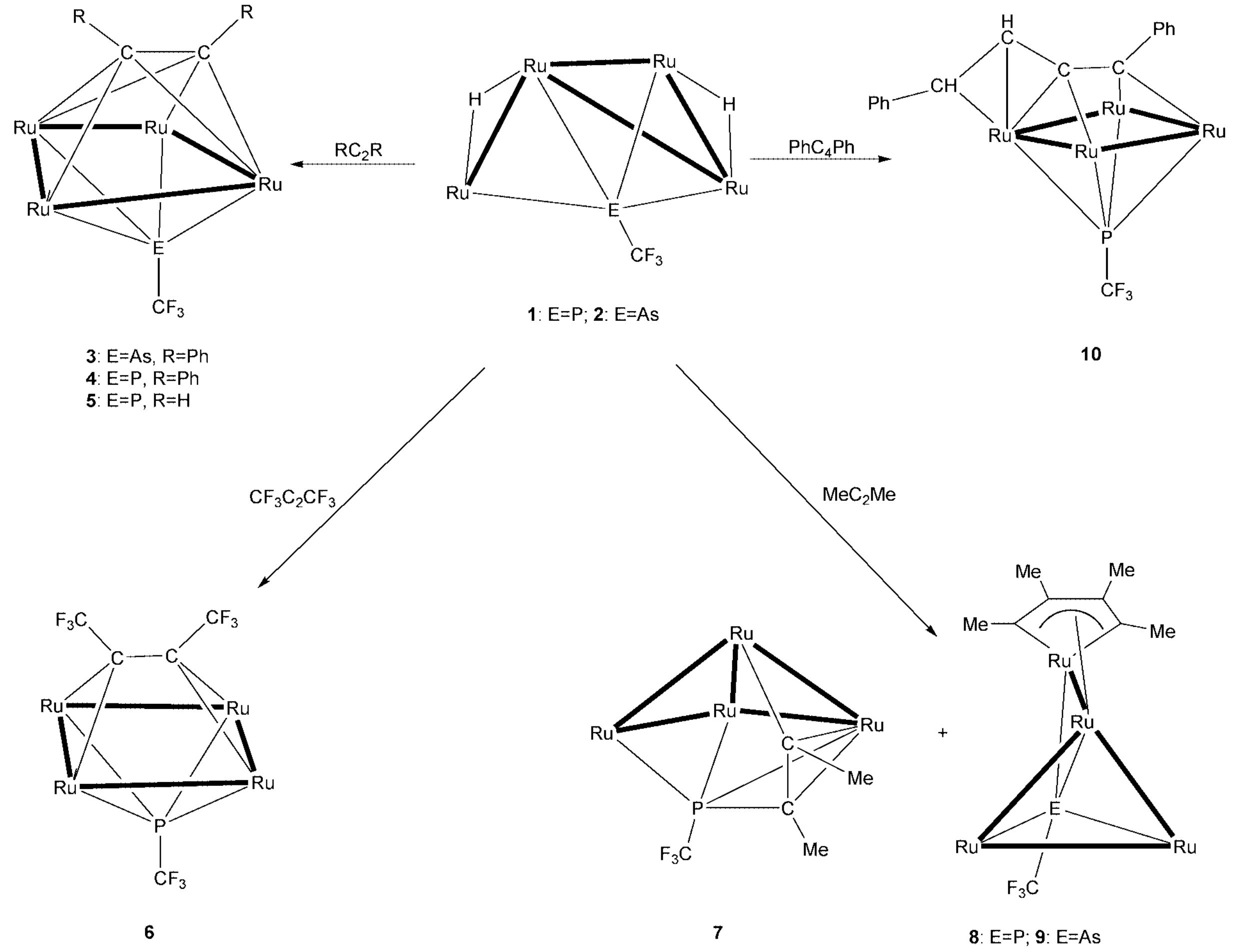
In the ^1H NMR spectra of compounds **3** and **4**, the resonances of *meta* and *para* protons of the phenyl groups appear at δ 6.74 and 6.76 and that of *ortho* hydrogen atoms at δ 6.10 and 6.03, showing a significant upfield shift compared to those of the "free" ligand. In the ^1H NMR spectrum of **5** the acetylenic protons show resonances at δ 5.37 and 5.41, which are close to those observed for the protons in ethene. The ^1H NMR of **7** displays a doublet at δ 2.66 with $J(PH) = 12.14$ Hz assigned to the methyl group near the phosphorus atom, while the other methyl resonance appears at lower field (δ 3.13) as a doublet with small coupling constant [$J(PH) = 2.55$ Hz].

The chemical shifts of the $^{31}P\text{-}\{H\}$ NMR signals of the electron deficient clusters **4** and **5** are markedly upfield compared to those of other clusters containing μ_4-phosphinidene ligands capping square faces in electron precise Ru_4 clusters. Electronic effects similar in nature to those of ring currents in aromatic systems have previously been cited as being responsible for this observation.[4] Thus the $\delta(^{31}P)$ values of 220.8 and 212.7 are in the region commonly encountered for 62 cluster valence

Table 1 The IR[a] and NMR[b] data for the new cluster derivatives

Cluster	$\tilde{\nu}$(CO)/cm^{-1}	NMR (δ, J/Hz) ^{1}H	^{31}P-{H}	^{19}F
3	2092w, 2062s, 2039s, 2014w, 1989m, 1854w	6.74 (m), 6.10 (m)		40.0 (s)
4	2094m, 2065s, 2042s, 2020w, 1993w, 1856w	6.76 (m), 6.03 (d)	220.8 (q), J(PF) = 85	32.7 (d)
5	2097w, 2064s, 2050s, 2040s, 2009m, 1994w, 1835w	5.41 (s), 5.37 (s)	212.7 (q), J(PF) = 85	32.8 (d)
6	2085s, 2053m, 2010w		414.1 (q), J(PF) = 78	26.6 (d), 28.9 (s)
7	2092w, 2067s, 2059m, 2034s, 1990w, 1975w	3.13 (d), 2.66 (d)	34.4 (qq), J(PF) = 69	17.5 (d)
8	2095w, 2076s, 2048s, 2036m, 2021m, 1998w, 1987w, 1932w, 1897w	2.09 (s), 2.77 (d)	194 (q), J(PF) = 51	31.1 (d)
9	2093w, 2074s, 2046s, 2034m, 2018m, 1998w, 1987w, 1928w, 1889w	2.26 (s), 2.06 (s)		35.9 (s)
10	2091w, 2067s, 2059m, 2033s, 2005w, 1997w, 1903w	7.18 (m), 4.35 (dd)	139.1 (q), J(PF) = 74	27.4 (d)

[a] In hexane. [b] In $CDCl_3$.



Scheme 1 Reactions of compounds **1** and **2** with alkynes and diphenylbutadiyne.

electrons (CVE) species of the type $[Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}X)(\mu_4\text{-}Y)]$.[5] However, **10**, a 64 CVE Ru_4 square cluster has a very upfield ^{31}P-{^{1}H} NMR signal at δ 139.1. In the case of the 64 CVE cluster **7** the ^{31}P-{H} NMR spectrum also displays a very high-field signal at δ 34.4. Such upfield shifts have been reported for other five-co-ordinate RR′P groups where the addition of one P–C bond in the change from a PR ligand to a PR(CMeCMe) group appears to have a major influence on δ_{iso}.[6] For such triply bridging phosphido ligands with overall five-co-ordinate stereochemistry at the phosphorus it has been observed that the Ru–P bond lengths are slightly longer than those associated with normal μ-phosphido-bridged clusters.[7]

Molecular structures of compounds 4 and 5

The molecular structure of **4**, together with some selected bond parameters is shown in Fig. 1. Crystallographic studies show that this cluster has a Ru_4 core arranged to be a distorted square plane with mean deviation from the plane being 0.16 Å. This Ru_4 square is capped on one side by a quadruply bridging phosphinidene ligand with almost equivalent Ru–P bond lengths [average 2.388(1) Å]. The diphenylacetylene is attached to the other side *via* a μ_4-η^2-bonding mode, with two σ bonds of C(3)–Ru(4) [2.207(3) Å] and C(4)–Ru(1) [2.147(3) Å] and four π co-ordinations to Ru(2) and Ru(3) *via* C(3) and C(4) with the bond lengths varying from 2.383(4) to 2.547(3) Å. The C(3)–C(4) bond distance is 1.400(4) Å, which is longer than a normal carbon–carbon double bond (1.334 Å) due to the π interactions with the metal skeleton. This kind of 2σ + 4π alkyne interaction with four metal atoms is common, but in most cases the metal atoms are not supported by any main group ligands like the planar clusters $[Ir_4(CO)_8\{C_2(COOMe)_2\}_4]$[8] and $[Ni_2Fe_2$-

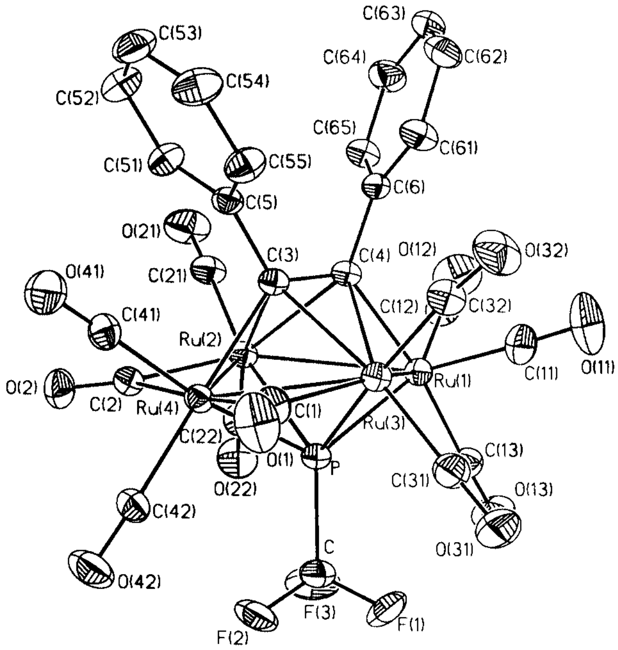


Fig. 1 Molecular structure of compound **4**. Bond lengths and angles which do not appear in the text: Ru(1)–P 2.345(1), Ru(2)–P 2.395(1), Ru(3)–P 2.413(1), Ru(4)–P 2.399(1), Ru(2)–C(3) 2.383(4), Ru(2)–C(4) 2.445(3), Ru(3)–C(3) 2.411(3) and Ru(3)–C(4) 2.547(3) Å; Ru(2)–Ru(1)–Ru(3) 81.9(1), Ru(1)–Ru(2)–Ru(4) 94.0(1), Ru(1)–Ru(3)–Ru(4) 94.4(1), Ru(2)–Ru(4)–Ru(3) 86.8(1), C(4)–C(3)–C(5) 119.6(3) and C(3)–C(4)–C(6) 117.4(3)°.

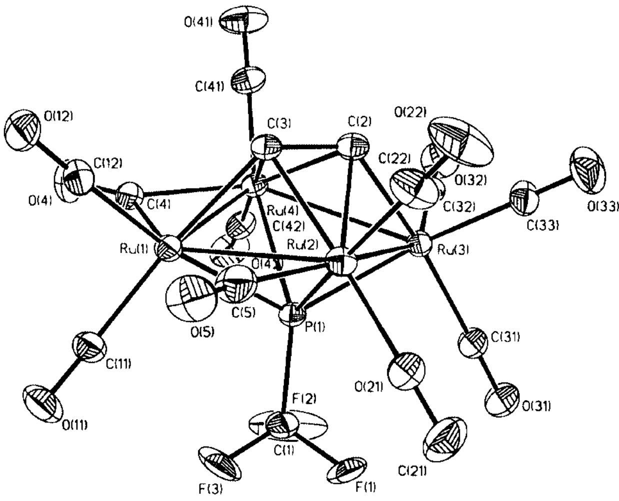


Fig. 2 Molecular structure of compound **5**. Important bond lengths and angles which do not appear in the text: Ru(1)–P(1) 2.389(2), Ru(2)–P(1) 2.420(2), Ru(3)–P(1) 2.358(2), Ru(4)–P(1) 2.470(2), Ru(1)–C(3) 2.153(6), Ru(2)–C(2) 2.359(7), Ru(2)–C(3) 2.305(6), Ru(3)–C(2) 2.111(7), Ru(4)–C(2) 2.421(7), Ru(4)–C(3) 2.342(6), Ru(3)–C(31) 1.972(7) and Ru(1)–C(11) 1.937(7) Å; Ru(2)–Ru(1)–Ru(4) 85.2(1), Ru(1)–Ru(2)–Ru(3) 93.9(1), Ru(2)–Ru(3)–Ru(4) 81.4(1) and Ru(1)–Ru(4)–Ru(3) 94.6(1)°.

$(\mathrm{Cp})_2(\mathrm{CO})_6(\mathrm{RC_2R'})$]],[9] and the four metal atoms often adopt a butterfly geometry as in the clusters $[\mathrm{Co_4(CO)_{10}(EtCCEt)}]$[10] and $[\mathrm{Ru_4(CO)_{12}(PhCCPh)}]$.[11] In cluster **4** each ruthenium atom is bonded to one terminal carbonyl group above the ruthenium plane and to one below the plane, except that the Ru(1) atom has an additional carbonyl ligand in the equatorial position. The remaining two, [C(1)O(1) and C(2)O(2)], bridge Ru(3)–Ru(4) and Ru(2)–Ru(4) respectively [Ru(3)–C(1) 2.034(3), Ru(4)–C(1) 2.136(4), Ru(2)–C(2) 2.008(3) Å, Ru(4)–C(2) 2.255 Å], and may be considered as bridging and semi-bridging carbonyls on the basis of the value $a = (d_2 - d_1)/d_1$, where d_2 is the longer Ru–C bond length and d_1 the shorter, being less (0.05) and greater (0.12) than 0.1 respectively, the value taken for practical purposes to be the boundary between bridging and semi-bridging carbonyl groups.[12] The existence of these bridging ligands reflects the electronic imbalance that would otherwise be associated with Ru(2), Ru(3) and Ru(4) in their absence. Cluster **4** contains only 62 valence electrons and so is formally electron deficient by 2 electrons.[13] In **4** two Ru–Ru bonds are similar and of normal length for Ru–Ru single bonds in tetranuclear clusters [Ru(1)–Ru(2) 2.896(1), Ru(1)–Ru(3) 2.900(1) Å] while the other two, those associated with the bridging carbonyl ligands, are appreciably shorter [Ru(2)–Ru(4) 2.775(1), Ru(3)–Ru(4) 2.755(1) Å] compared to the standard Ru–Ru single bond in $[\mathrm{Ru_3(CO)_{12}}]$ (2.8555 Å).[14] This shortening could be due to the existence of a localized multiple bond or the influence of the bridging carbonyl ligand.

A diagram of the molecular structure of compound **5** together with some selected bond lengths and angles is shown in Fig. 2. Cluster **5** has a similar structure to that of **4** but contains a more distorted square $\mathrm{Ru_4}$ plane with the mean deviation being 0.21 Å. The acetylene ligand is attached to the $\mathrm{Ru_4}$ square face through σ interactions [Ru(1)–C(3) 2.153(6); Ru(3)–C(2) 2.111(7) Å] and π interactions [Ru(2)–C(3) 2.305(6), Ru(4)–C(3) 2.342(6), Ru(2)–C(2) 2.359(7), Ru(4)–C(2) 2.421(7) Å], with a μ_4-$\mathrm{PCF_3}$ ligand supporting the apical position.

The overall structure of compound **5** is analogous to that of **4**, but there are still some structural variances between them. First, the alkyne–$\mathrm{Ru_4}$ interaction in **5** is a little stronger than that in **4** since the average Ru–C (acetylenic carbon) bond length of **5** is 2.282(7) Å, which is 0.075 Å shorter than that of **4**. This difference is probably because the small hydrogen substituents in acetylene may allow it to approach more closely to the metal framework than diphenylacetylene. Secondly, the metal skeleton of **5** reveals a different distribution of Ru–Ru bonds from that of **4**, with the pattern of three normal [Ru(1)–Ru(2) 2.834(2), Ru(2)–Ru(3) 2.864(2) and Ru(3)–Ru(4) 2.920(2) Å] and one shortened [Ru(1)–Ru(4) 2.740(1) Å]. Besides, the distribution of bridging carbonyl ligands is also different from that of **4**. In cluster **5** one carbonyl ligand is bridging the shortest Ru–Ru bond with equivalent Ru–C bond length [2.067(7) Å] while the other, leaning slightly towards the Ru(1) atom, can be considered as linear semi-bridging based on the following two facts: (i) the ratio of the longer [Ru(1)–C(5) 2.625(7) Å] to the shorter [Ru(2)–C(5) 1.954(8) Å] ruthenium–carbon distances (1.3 : 1) is within the range $1.1 < a < 1.6$ which Curtis regards as the "semi-bridging" region;[12] (ii) the θ value [Ru(2)–C(5)–O(5) 160.3(8)°] falls in the range 160–180° with ψ [Ru(1)–Ru(2)–C(5)] being 63.4°, showing the linear semi-bridging characteristic.[15] This linear semi-bridging carbonyl involves electron donation from the CO π orbitals to Ru(1) to relieve electron deficiency at Ru(1).[16] Similar linear type carbonyl bridges are found in $[\mathrm{Fe_3(CO)_8(C_4H_8S)_2}]$ and $[\mathrm{Os_3(CO)_{10}}$-$(\mathrm{PhC_2Ph})]$ where the M–C–O angles are 167.4(7) and 166.6(9)° respectively.[17]

Molecular structure of compound 6

As illustrated in Fig. 3, cluster **6** consists of a square planar $\mathrm{Ru_4}$ skeleton with all the ruthenium atoms almost being coplanar (the largest deviation from the least squares plane is 0.018 Å). If the carbon atoms of the acetylene are considered to be the vertices of the cluster polyhedron, the geometry of **6** can be regarded as a trigonal prism or tetragonally $\mathrm{CF_3P}$-capped trigonal prism. The distances of three Ru–Ru bonds [2.807(2)–2.886(2) Å] are normal and the fourth [2.917(2) Å] slightly elongated. This M–M bond contribution is quite different from that of a series of similar complexes like clusters **4** or **5** where the pattern of two short and two normal Ru–Ru bonds or three normal and one short Ru–Ru bond was found. This difference is consistent with the different total valence electrons of the clusters. For **6** the total valence electrons is 64 and it can be classified as an electron precise cluster. All the carbon

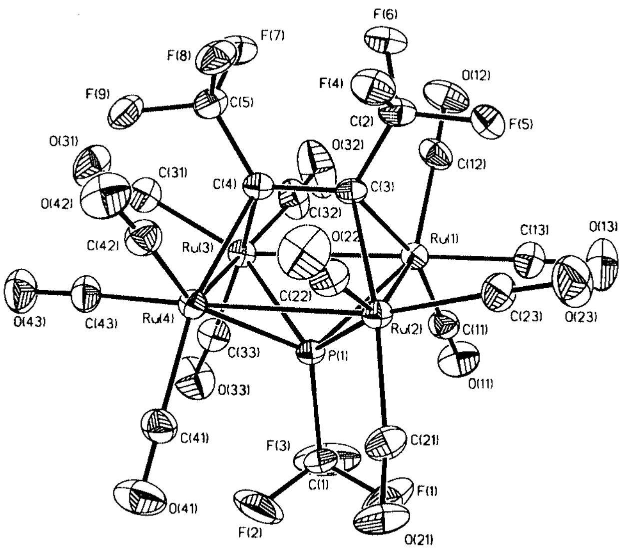


Fig. 3 Molecular structure of compound **6**. Important bond lengths and angles which do not appear in the text: Ru(1)–Ru(2) 2.862(2), Ru(1)–Ru(3) 2.917(2), Ru(2)–Ru(4) 2.886(2), Ru(3)–Ru(4) 2.807(2), Ru(1)–P(1) 2.362(2), Ru(2)–P(1) 2.367(2), Ru(3)–P(1) 2.349(2), Ru(4)–P(1) 2.341(2), Ru(1)–C(3) 2.164(6), Ru(2)–C(3) 2.165(6), Ru(3)–C(4) 2.180(6) and Ru(4)–C(4) 2.210(6) Å; Ru(1)–Ru(2)–Ru(4) 89.0(1), Ru(1)–Ru(3)–Ru(4) 89.4(1), Ru(2)–Ru(1)–Ru(3) 89.9(1), Ru(2)–Ru(4)–Ru(3) 91.7(1), C(3)–C(4)–C(5) 119.8(5) and C(2)–C(3)–C(4) 121.0(5)°.

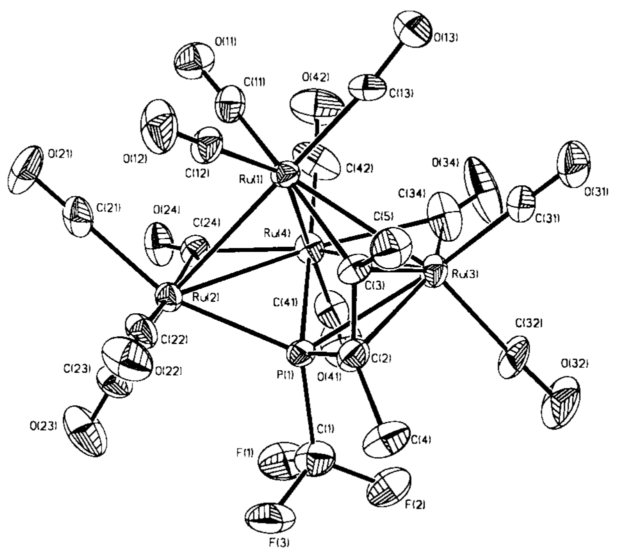


Fig. 4 Molecular structure of compound **7**. Important bond lengths and angles which do not appear in the text: Ru(1)–Ru(2) 2.906(2), Ru(1)–Ru(3) 2.872(2), Ru(1)–Ru(4) 2.864(1), Ru(2)–Ru(4) 2.883(1), Ru(3)–Ru(4) 2.784(2), Ru(2)–P(1) 2.316(4), Ru(3)–P(1) 2.513(4) and Ru(4)–P(1) 2.436(4) Å; Ru(2)–Ru(1)–Ru(3) 95.7(1), Ru(2)–Ru(1)–Ru(4) 60.0(1), Ru(3)–Ru(1)–Ru(4) 58.1(1), Ru(1)–Ru(2)–Ru(4) 59.3(1), Ru(1)–Ru(4)–Ru(2) 60.7(1), Ru(1)–Ru(4)–Ru(3) 61.1(1), Ru(2)–Ru(4)–Ru(3) 98.2(1), C(2)–C(3)–C(5) 119.3(12) and C(3)–C(2)–C(4) 126.2(13)°.

monoxides attached to the Ru atoms are nearly linear, giving an average Ru–C–O angle of 176°.

Cluster **6** contains a multisite-bound acetylenic ligand. The acetylenic C(3)–C(4) bond, which possesses a μ_4-η^2-co-ordination mode, lies at the top of the Ru_4 square face. However, unlike **4** and **5**, where the acetylene ligands are co-ordinated to the Ru_4 planes *via* $2\sigma + 4\pi$ bonds, the hexafluorobutyne interacts with four Ru atoms apparently only *via* σ bonds. On the other hand, the different co-ordination mode between clusters **6** and **4** or **5** is also reflected in the different orientations of the acetylene ligands. As illustrated in cluster **4** (Fig. 1), the acetylene ligand is parallel to the diagonal Ru(1) · · · Ru(4) vector while in **6** it is almost parallel to Ru(1)–Ru(2) and Ru(1)–Ru(3) bonds and approximately perpendicular to the Ru(2)–Ru(3) and Ru(3)–Ru(4) edges. Among the complexes in which the alkyne interacts with more than four metal atoms are a small number of clusters containing alkynes in co-ordination mode similar to that of **6**, as exemplified by $[Ir_4(CO)_8\{C_2(COOMe)_2\}_4]$.[10] In this sort of co-ordination mode the hexafluorobutyne donates four electrons to the Ru_4 plane making four M–C bonds with the separations varying in a narrow range [2.164(6) to 2.210(6) Å]. The acetylenic carbon C(3) is connected to Ru(1) and Ru(2) almost symmetrically whereas the other C(4) bridges Ru(2) and Ru(4) a little asymmetrically. It is worth noting that the acetylenic C–C bond in **6** [1.510(8) Å] has been reduced to a greater extent than those reported for $[Ir_4(CO)_8\{C_2(COOMe)_2\}_4]$ [1.446(4) Å] and many other M_4 clusters with μ_4-η^2-non-fluorinated alkynes. The elongation of the C(3)–C(4) bond thus reflects an extensive rehybridization of the carbon atoms to fulfil the bonding requirements.

Molecular structure of compound 7

X-Ray analysis shows that cluster **7** consists of a butterfly arrangement of ruthenium atoms, or [if the phosphorus atom is considered as one of the basal vertex atoms] a square-pyramidal Ru_4P arrangement (Fig. 4). Five normal Ru–Ru single bonds [average 2.862(2) Å] form the butterfly with the dihedral angle between the wings being 119.8°. The acetylene ligand is bonded to the Ru(1)–Ru(3)–P(1) triangular face in a μ_3-η^2 mode. The acetylenic carbons co-ordinate to phosphorus and Ru(1) with σ bonds [Ru(1)–C(3) 2.159(13), P(1)–C(2) 1.788(15) Å], whereas to Ru(3) *via* a π interaction [Ru(3)–C(3) 2.261(13), Ru(3)–C(2) 2.318(15) Å], donating three electrons to the cluster core. The π bonded Ru–C distance (mean value 2.29 Å) is a little shorter than that of **4** (2.447 Å) and **5** (2.357 Å). The acetylenic C(2)–C(3) bond length [1.390(19) Å] is in the range of values for μ_4-η^2-alkynes. The MeC_2Me deviates slightly from planarity (torsion angle −2.2°) and the MeC_2Me framework is quite asymmetric, with the angle C(2)–C(3)–C(5) [119.3(12)°] being smaller than C(3)–C(2)–C(4) [126.2(13)°]. Ten of twelve carbonyl ligands in **7** are terminally bonded to the ruthenium atoms, the remaining two symmetrically bridge Ru(2)–Ru(4) and Ru(4)–Ru(3) respectively.

Molecular structure of compounds 8 and 9

According to X-ray diffraction analyses, clusters **8** and **9** are isostructural, with each containing a spiked metal arrangement supported by a μ_4-ECF_3 (E = P, As) ligand (Figs. 5 and 6). The molecular structure contains a crystallographic mirror plane passing through two Ru atoms, the ECF group and a CO ligand (in the case of **8**, these are the Ru(1), Ru(3), P, C, F(2), C(32) and O(32) atoms and the plane is vertical to the Ru(2)–Ru(2a) and C(3)–C(3a) bonds). The bonding between the Me_4C_4 fragment and the cluster is attained *via* σ bonds of Ru(3) with C(2) and C(2a) and a donation of the four π electrons of the metallacyclopentadiene ring to Ru(1) (in **8**, Ru(1)–C(2) 2.218(4), Ru(1)–C(3) 2.280(5) Å). Thus, the Me_4C_4 moiety donates a total of six electrons to the whole cluster.

The crystal structures of clusters **8** and **9** show that they each contain two semi-bridging carbonyl groups. In the case of **8** the carbonyl groups on the Ru(1) atom (namely C(12)O(12) and C(12a)O(12a)) which lean towards the Ru(2) and Ru(2a) atoms, could be classified as semi-bridging on the grounds that the ratio of the Ru(2)–C(12) distance [2.519(5) Å] to that of Ru(1)–C(12) distance [1.889(6) Å] is 1.3 : 1. The distances of the Ru–Ru bonds associated with the bridging carbonyl ligands are longer [2.843(1) Å] than that of non-bridging Ru(2)–Ru(2a) [2.764(1) Å]. This distribution is in contrast to those observed for the electron deficient clusters **4** and **5** and even other electron precise clusters where the bridging carbonyl ligands usually bridge

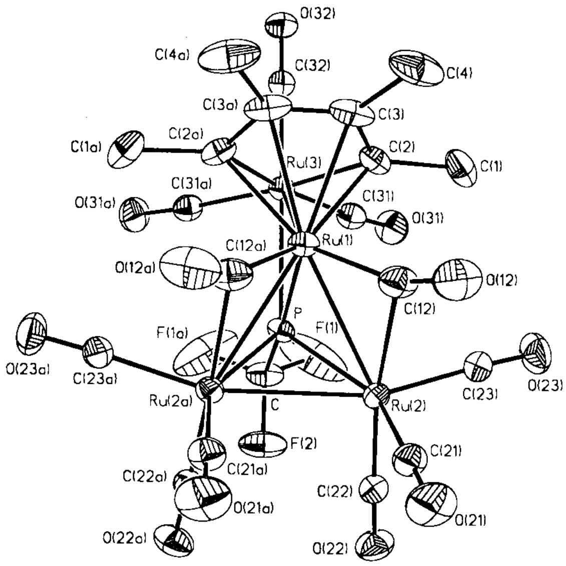


Fig. 5 Molecular structure of compound **8**. Important bond lengths and angles which do not appear in the text: Ru(1)–Ru(2) 2.843(1), Ru(2)–Ru(2a) 2.764(1), Ru(1)–P 2.494(2), Ru(2)–P 2.330(1), Ru(3)–P 2.532(1), Ru(1)–C(2) 2.218(4), Ru(1)–C(3) 2.280(5), Ru(3)–C(2) 2.117(5), C(2)–C(3) 1.438(6) and C(3)–C(3a) 1.376(12) Å; Ru(2)–Ru(1)–Ru(3) 100.2(1), Ru(2)–Ru(1)–Ru(2a) 58.2(1), Ru(1)–Ru(2)–Ru(2a) 60.9(1), Ru(3)–C(2)–C(3) 114.0(3), C(2)–C(3)–C(3a) 116.0(3) and C(2)–Ru(3)–C(2a) 77.0(2)°.

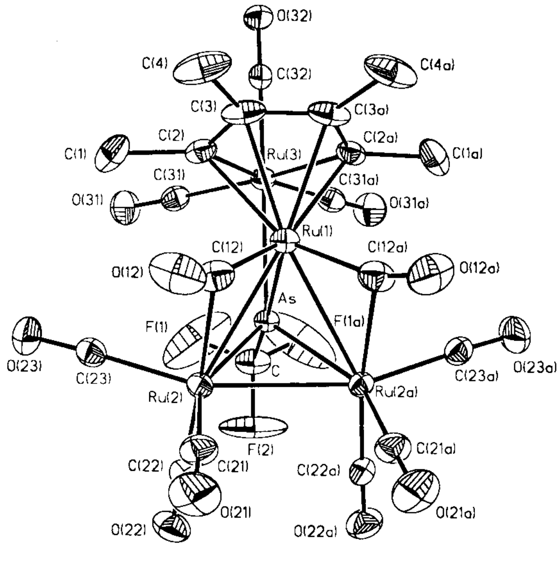


Fig. 6 Molecular structure of compound **9**. Important bond lengths and angles which do not appear in the text: Ru(1)–Ru(2) 2.870(1), Ru(1)–Ru(3) 2.797(1), Ru(2)–Ru(2a) 2.780(1), Ru(1)–As 2.579(1), Ru(2)–As 2.422(1), Ru(3)–As 2.595(1), Ru(1)–C(2) 2.225(6), Ru(1)–C(3) 2.268(6), Ru(3)–C(2) 2.123(6), C(2)–C(3) 1.406(8) and C(3)–C(3a) 1.449(15) Å; Ru(2)–Ru(1)–Ru(3) 101.7(1), Ru(2)–Ru(1)–Ru(2a) 57.9(1), Ru(1)–Ru(2)–Ru(2a) 61.0(1), Ru(3)–C(2)–C(3) 116.0(4), C(2)–C(3)–C(3a) 114.6(4) and C(2)–Ru(3)–C(2a) 76.1(3)°.

the shorter Ru–Ru bonds. The existence of the semi-bridging carbonyls in **8** reflects the formal electron imbalance within the metal framework; Ru(2) is formally associated with 17 electrons, Ru(1) with 20 electrons, and Ru(3) is electron precise with 18 electrons. The existence of the semi-bridging carbonyl ligands thus redistributes the electrons within the metal triangle. Overall, the C_4 chain contributes six electrons to the cluster core in which the Ru(3) atom accepts two electrons and Ru(1) the rest. In terms of electron counting **8** is a 64-electron cluster, consistent with the presence of four metal–metal bonds. The semi-bridging carbonyl ligands bend away quite a lot against the phosphinidene group with the dihedral angle between the Ru(1)Ru(2)Ru(3) and Ru(1)Ru(2)C(12) triangles being 127.3°.

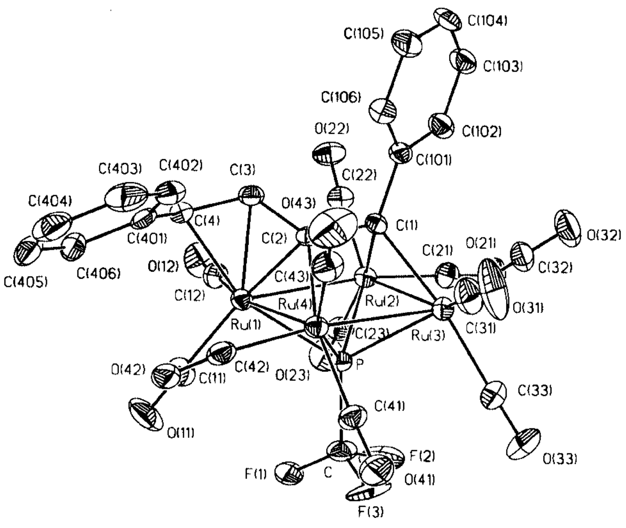


Fig. 7 Molecular structure of compound **10**. Important bond lengths and angles which do not appear in the text: Ru(1)–Ru(2) 2.922(2), Ru(1)–Ru(4) 2.851(2), Ru(2)–Ru(3) 2.827(2), Ru(3)–Ru(4) 2.888(2), Ru(1)–P 2.353(2), Ru(2)–P 2.377(2), Ru(3)–P 2.398(3), Ru(4)–P 2.363(3), Ru(1)–C(2) 2.153(7), Ru(1)–C(3) 2.215(7), Ru(1)–C(4) 2.297(7), Ru(3)–C(1) 2.169(6) and Ru(4)–C(2) 2.164(6) Å; Ru(1)–Ru(2)–Ru(3) 91.2(1), Ru(2)–Ru(1)–Ru(4) 88.0(1), Ru(2)–Ru(3)–Ru(4) 89.2(1), Ru(1)–Ru(4)–Ru(3) 91.4(1), C(1)–C(2)–C(3) 121.0(5) and C(2)–C(3)–C(4) 124.6(6)°.

Another interesting feature in the structure is the significantly shorter distance between Ru(1) and Ru(2) [2.757(1) Å] compared to those in $[Ru_3(CO)_{12}]$ (2.855 Å). Two bridging CO ligands are also present in **9**, and these are bent away from the arsinidene ligand making a dihedral angle between the triruthenium and Ru(1), Ru(2), C(12) planes of 127.3°. This again demonstrates the redistribution of electron density from electron-rich Ru(1) to electron-poor Ru(2).

There are some structural differences between clusters **8** and **9**. For example, the average Ru–Ru bond length in **9** is 2.816 Å which is slightly longer than 2.788 Å in **8**. Also, the bond patterns of the metallacyclic rings in **8** and **9** are different. Cluster **8** gives two long [C(2)–C(3) 1.438(6) Å] and a short C–C bond [C(3)–C(3a) 1.376(12) Å], which is comparable to a double bond. The metallacyclic ring of **9** reveals a reverse distribution of C–C bonds, with two short [C(2)–C(3) 1.406(8) Å] and one long [C(3)–C(3a) 1.449(15) Å], which is an intermediate value between a C–C single bond length and C=C double bond length. In both cases, the bond angles within the ring are nearly 120° and thus this metallacyclic system can be viewed as a somewhat delocalized diene with the Ru(3) σ bonded to two carbon atoms C(2) and C(2a) [Ru(3)–C(2) 2.117(5) Å for **8** and 2.123(6) Å for **9**].

Molecular structure of compound 10

The molecular structure of compound **10** (Fig. 7) shows a Ru_4 square structure containing the CF_3P fragment on one side and the 1,4-diphenylbut-3-en-1-yne ligand attached to the opposite side. The Ru_4 square is more planar (mean deviation 0.03 Å) compared to that of **4** and **5** but less than that in **6**. The metal–carbon distances associated with the alkyne [average 2.172(7) Å] are slightly shorter than in the olefin moiety [average 2.256(7) Å]. The acetylenic triple bond C(1)–C(2), which possesses a μ_4-η^2 bonding mode, donates four electrons to the metal square making four Ru–C bonds with lengths varying in a narrow range [2.153(7)–2.201(8) Å]. The C(2) atom is connected to Ru(1) and Ru(4) nearly symmetrically while C(1) bridges Ru(2) and Ru(3) a little asymmetrically. This coordination mode is very similar to that observed in **6** and the four Ru–C contacts are better considered as σ bonds despite the distance Ru(2)–C(1) [2.201(8) Å] being relatively long. In the C_4

Table 2 Crystallographic data for the new cluster derivatives

	4	**5**	**6**	**7**	**8**	**9**	**10**
Formula	$C_{26}H_{10}F_3O_{11}PRu_4$	$C_{14}H_2F_3O_{11}PRu_4$	$C_{17}F_9O_{12}PRu_4$	$C_{17}H_6F_3O_{12}PRu_4$	$C_{20}H_{12}F_3O_{11}PRu_4$	$C_{20}H_{12}AsF_3O_{11}Ru_4$	$C_{28}H_{12}F_3O_{11}PRu_4$
M	990.6	840.4	1002.4	894.5	920.5	964.5	1016.6
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$Pbca$	$Pnma$	$Pnma$	$P\bar{1}$
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic
a/Å	9.288(2)	10.046(4)	9.317(6)	9.615(5)	17.761(4)	17.959(3)	10.115(6)
b/Å	9.689(2)	14.858(6)	18.024(11)	16.597(5)	14.422(3)	14.353(3)	12.223(8)
c/Å	17.722(4)	14.673(7)	15.345(8)	31.303(13)	10.376(2)	10.460(3)	14.464(10)
α/°	91.76(3)						81.07(5)
β/°	91.22(3)	90.47(4)	92.48(4)				77.50(5)
γ/°	110.03(3)						68.98(5)
U/Å^3	1496.9(8)	2190.1(16)	2575.0(2)	4995(3)	2659.6(13)	2696.4(10)	1644(2)
Z	2	4	4	8	4	4	2
Measured independent reflections	6985/6589	4039/3813	4635/4362	4191/4191	2975/2975	2385/2385	5796/5796
R(int)	1.44	3.18	3.48	0	0	0	0
μ/cm^{-1}	2.11	2.86	2.49	2.52	2.36	3.49	1.92
Final $R(R')$	0.0236(0.0391)	0.0426(0.0601)	0.0426(0.0666)	0.0569(0.0695)	0.0272(0.0475)	0.0278(0.0441)	0.0430(0.0682)

backbone the bond C(1)–C(2) [1.497(9) Å] is significantly longer than that of its phenylphosphine analogue $[Ru_4(CO)_{12}(\mu_4\text{-PPh})\{PhC(H)C(H)CCPh\}]$[9] [1.422(13) Å], while the lengths of the other two C–C bonds are nearly equal [C(2)–C(3) 1.429(8); C(3)–C(4) 1.427(10) Å]. The C_4 backbone including the ruthenium-olefin interactions, acts as a six electron donor to the cluster.

Conclusion

Spiked clusters $[Ru_4(CO)_{13}(\mu\text{-H})_2(\mu_4\text{-ECF}_3)]$ (E = P **1** or As **2**) are found to react with alkynes to give a variety of cluster derivatives. Alkynes PhCCPh and HCCH give similar derivatives **3**, **4** and **5** where the alkyne ligands are attached to the Ru_4 square *via* a $2\sigma + 4\pi$ co-ordination mode. However, the reactions with CF_3CCCF_3 [containing electronegative CF_3 groups] give **6** where the alkyne ligand is attached to the Ru_4 square *via* only 4σ bonds. Furthermore, treatment of **1** and **2** with MeCCMe yields a butterfly cluster derivative **7** and spiked cluster derivatives **8** and **9**, whereby metal skeletal rearrangement from spiked to butterfly, formation of a P–C (acetylene) bond and dimerization of the alkyne at the spiked Ru atom occur. Reaction of **1** with diphenylbutadiyne gives the square planar cluster derivative **10**, where the bridging hydrogen migrates from the cluster to the diyne to form a 1,4-diphenylbut-3-en-yne fragment. In the cluster derivatives obtained the CO ligands also display bridging, bent semi-bridging and linear semi-bridging structures.

Experimental

All synthetic reactions were carried out under vacuum. Solvents were distilled under nitrogen over appropriate drying agents. Commercially available alkynes and diphenylacetylene were used without further purification. Clusters **1** and **2** were prepared according to ref. 18. The IR spectra were recorded using a Perkin-Elmer 1600 FT-IR spectrophotometer, NMR spectra using a Bruker ACF-300 or a JEOL FX-90Q FT spectrometer.

Suitable crystals for X-ray crystallographic studies were obtained from CH_2Cl_2–hexane solution at −20 °C. Intensity data were collected on a Siemens R3m/V diffractometer at room temperature. Table 2 summarizes the crystallographic and selected experimental data for the complexes. The structures were solved by direct methods using the SHELXTL PLUS PC program package,[19] full-matrix least-squares refinement on *F* with anisotropic displacement factors for non-H atoms; hydrogen atoms we located in idealized positions and not refined.

CCDC reference number 186/1575.

Syntheses

$[Ru_4(CO)_9(\mu\text{-CO})_2(\mu_4\text{-PCF}_3)(PhC_2Ph)]$ 4. The compound **1** (80 mg, 0.092 mmol) and PhC≡CPh (50 mg, 0.28 mmol) were placed in a reaction vessel with 5 ml degassed *p*-xylene. The mixture was then allowed to react at 70 °C for 18 h. After removing the solvent in vacuum, the residue was dissolved in the minimum volume of CH_2Cl_2 and TLC using pentane as eluent afforded **4** ($R_f = 0.33$; 30 mg, 33%) (Found: C, 31.55; H, 1.21; P, 3.40. Calc. for $C_{26}H_{10}F_3O_{11}PRu_4$: C, 31.51; H, 1.01; P, 3.10%).

$[Ru_4(CO)_9(\mu\text{-CO})_2(\mu_4\text{-PCF}_3)(HC_2H)]$ 5. A solution of compound **1** (80 mg, 0.092 mmol) in 5 ml of *p*-xylene was degassed and HCCH (7.18 mg, 0.28 mmol) condensed in at liquid nitrogen temperature. The mixture was heated at 70 °C for 24 h, after which the solvent was removed in vacuum. The residue was extracted into CH_2Cl_2 and separated *via* TLC (hexane as eluent), yielding **5** ($R_f = 0.14$; 14 mg, 18%) (Found: C, 20.25. Calc. for $C_{14}H_2F_3O_{11}PRu_4$: C, 19.98%).

$[Ru_4(CO)_9(\mu\text{-CO})_2(\mu_4\text{-AsCF}_3)(PhC_2Ph)]$ 3. The reaction was similar to that described for compound **4**. Cluster **2** (77 mg, 0.084 mmol) was treated with diphenylacetylene (45 mg, 0.25 mmol). Separation by TLC afforded **3** ($R_f = 0.41$; 18 mg, 21%) (Found: C, 30.12, As, 7.24. Calc. for $C_{24}H_{10}AsF_3O_{11}Ru_4$: C, 30.17; As, 7.24%).

$[Ru_4(CO)_{12}(\mu_4\text{-PCF}_3)(CF_3C_2CF_3)]$ 6. A solution of compound **1** (140 mg, 0.16 mmol) in cyclohexane was degassed and then hexafluorobutyne (77.76 mg, 0.48 mmol) was condensed in at liquid nitrogen temperature. The mixture was allowed to react at 70 °C over 18 h during which a change from yellow to red occurred. After removal of the volatile components and solvent, the resulting solid was dissolved in CH_2Cl_2 and absorbed onto TLC plates. Elution with hexane afforded **6** ($R_f = 0.33$; 26 mg, 16%) (Found: C, 20.27; P, 3.09. Calc. for $C_{17}O_{12}F_9PRu_4$: C, 20.35; P, 3.09%).

$[Ru_4(CO)_{10}(\mu\text{-CO})_2\{CF_3PC(Me)C(Me\}]$ 7 and $[Ru_4(CO)_9(\mu\text{-CO})_2(\mu_4\text{-PCF}_3)(C_4Me_4)]$ 8. The compound **1** (80 mg, 0.092 mmol) was degassed with 10 ml *p*-xylene and then MeCCMe (14.90 mg, 0.28 mmol) introduced at −198 °C under vacuum. The mixture was allowed to react at 70 °C with stirring for 18 h during which it was changed from yellow to brown. The solution was evaporated and chromatographed on silica gel plates using hexane as eluent to yield two major bands of **7** ($R_f = 0.38$; 17 mg, 20%) (Found: C, 23.66; H, 0.79; F, 6.16; P, 2.87. Calc. for $C_{17}H_6F_3O_{12}PRu_4$: C, 22.81; H, 0.67; F, 6.37; P, 3.47%) and **8** ($R_f = 0.15$, 12 mg, 15%) (Found: C, 26.22; H, 1.33; F, 6.29; P, 3.71. Calc. for $C_{20}H_{12}F_3O_{11}PRu_4$: C, 26.08; H, 1.30; F, 6.19; P, 3.37%).

$[Ru_4(CO)_9(\mu\text{-CO})_2(\mu_4\text{-AsCF}_3)(C_4Me_4)]$ 9. The synthetic method is similar to that for compound **9**. A mixture of compound **2** (60 mg, 0.065 mmol) and MeCCMe (10.53 mg, 0.20 mmol) was heated at 70 °C for 18 h. Purification gave **9** ($R_f = 0.23$; 11.3 mg, 18%) (Found: C, 24.93; H, 1.20; As, 7.32. Calc. for $C_{20}H_{12}AsF_3O_{11}Ru_4$: C, 24.88; H, 1.24; As, 7.77%).

$[Ru_4(CO)_{11}(\mu_4\text{-PCF}_3)\{PhC(H)C(H)CCPh\}]$ 10. A mixture of compound **1** (80 mg, 0.092 mmol) and diphenylacetylene (37.17 mg, 0.18 mmol) in 5 ml degassed *p*-xylene was heated at 70 °C for 17 h. The resulting dark red solution was separated by TLC to afford **10** ($R_f = 0.33$; 26 mg, 28%) (Found: C, 33.01; H, 1.12; F, 5.11; P, 2.89. Calc. for $C_{28}H_{12}F_3O_{11}PRu_4$: C, 33.06; H, 1.18; F, 5.61; P, 3.05%).

Acknowledgements

We thank the National University of Singapore for financial support and for a Research Scholarship to D. S.

References

1 E. Sappa, A. Tiripicchio, A. J. Carty and G. E. Toogood, *Prog. Inorg. Chem.*, 1987, **35**, 437.

2 J. Lunniss, S. A. MacLaughlin, N. J. Taylor, A. J. Carty and E. Sappa, *Organometallics*, 1985, **4**, 2066.

3 J. F. Corrigan, N. J. Taylor and A. J. Carty, *Organometallics*, 1994, **13**, 3778; J. F. Corrigan, S. Doherty, N. J. Taylor and A. J. Carty, *Organometallics*, 1992, **11**, 3160; 1993, **12**, 1365.

4 K. Eichele, R. E. Wasylishen, J. F. Corrigan, N. J. Taylor and A. J. Carty, *J. Am. Chem. Soc.*, 1995, **117**, 6961.

5 F. van Gastel, L. Agocs, A. A. Cherkas, J. F. Corrigan, S. Doherty, R. Ramachandran, N. J. Taylor and A. J. Carty, *J. Cluster Sci.*, 1991, **2**, 131; P. Braunstein, *New J. Chem.*, 1986, **10**, 365; R. D. Adams, T. A. Wolfe and W. Wu, *Polyhedron*, 1991, **10**, 447; P. Mathur, B. H. S. Thimmappa and A. L. Rheingold, *Inorg. Chem.*, 1990, **29**, 4658; R. D. Adams, J. E. Babin and M. Tasi, *Inorg. Chem.*, 1986, **25**, 4514; R. D. Adams, J. E. Babin, J. Estrads, J. G. Wang, M. B. Hall and A. A. Low, *Polyhedron*, 1989, **8**, 1885; P. Mathur, L. J. Mavunkal, V. Rugmini and M. F. Mahon, *Inorg. Chem.*, 1990, **29**, 4838; P. Mathur, D. Charkrabarty and M. M. Hossain, *J. Organomet. Chem.*, 1991, **418**, 415.

6 J. F. Corrigan, S. Doherty, N. J. Taylor and A. J. Carty, *J. Am. Chem. Soc.*, 1992, **114**, 7557.

7 A. J. Carty, S. A. MacLaughlin and D. Nucciarone, *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*: *Organic Compounds and Metal Complexes*, eds. J. G. Verkade and L. D. Quinn, VCH, New York, 1987, ch. 16, p. 605.

8 P. F. Heveldt, B. F. G. Johnson, J. Lewis, P. R. Raithby and G. M. Sheldrick, *J. Chem. Soc.*, *Chem. Commun.*, 1978, 340.

9 E. Sappa, A. Tiripicchio and M. T. Camellini, *J. Organomet. Chem.*, 1980, **199**, 243; G. Jaouen, A. Marinetti, B. Mentzen, R. Mutin, J. Y. Saillard, B. G. Sayer and M. J. MaGlinchey, *Organometallics*, 1982, **1**, 753; G. Jaouen, A. Marinetti, B. Mentzen, R. Mutin, J. Y. Saillard, B. G. Sayer and M. J. MaGlinchey, *Organometallics*, 1982, **1**, 225.

10 L. F. Dahl and D. L. Smit, *J. Am. Chem. Soc.*, 1962, **84**, 26.

11 B. F. G. Johnson, J. Lewis, B. E. Reichert, K. T. Schorpp and G. M. Sheldrick, *J. Chem. Soc.*, *Dalton Trans.*, 1977, 1417.

12 M. D. Curtis, K. R. Han and W. M. Butler, *Inorg. Chem.*, 1980, **19**, 2096.

13 C. R. Eady, B. F. G. Johnson and J. Lewis, *J. Chem. Soc.*, *Dalton Trans.*, 1975, 2606.

14 M. R. Churchill, F. J. Hollander and J. P. Hutchinson, *Inorg. Chem.*, 1977, **16**, 2655.

15 R. H. Crabtree and M. Lavin, *Inorg. Chem.*, 1986, **25**, 805.

16 R. J. Klingler, W. M. Butler and D. Curtis, *J. Am. Chem. Soc.*, 1978, **100**, 5034.

17 F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, 1974, **96**, 5070; C. G. Pierpont, *Inorg. Chem.*, 1977, **16**, 636.

18 C. T. Sears and F. G. A. Stone, *J. Organomet. Chem.*, 1968, **11**, 644.

19 G. M. Sheldrick, SHELXTL PLUS, Siemens Analytical Instruments, Madison, WI, 1986.

Paper 9/02963J