

# Reactions of trifluoromethyl-phosphine and -arsine with a ruthenium carbonyl cluster: synthesis, characterization and reactivity of cluster derivatives capped by trifluoromethyl-phosphinidene and -arsinidene moieties

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Received 31st March 1999, Accepted 2nd July 1999

Reactions of  $\text{CF}_3\text{EH}_2$  ( $\text{E} = \text{P}$  or  $\text{As}$ ) with  $[\text{Ru}_3(\text{CO})_{12}]$  under various conditions resulted in the elimination of two hydrogen atoms to afford new trifluoromethyl-phosphinidene and -arsinidene capped ruthenium carbonyl clusters:  $[\text{Ru}_3(\text{CO})_9(\mu\text{-H})_2(\mu_3\text{-PCF}_3)]$  **1**,  $[\text{Ru}_4(\text{CO})_{13}(\mu\text{-H})_2(\mu_4\text{-PCF}_3)]$  **2**,  $[\text{Ru}_4(\text{CO})_{12}(\mu\text{-H})_2(\mu_3\text{-PCF}_3)_2]$  **3**,  $[\text{Ru}_5(\text{CO})_{15}(\mu\text{-H})_2(\mu_3\text{-PCF}_3)_3]$  **4**,  $[\text{Ru}_5(\text{CO})_{15}(\mu_4\text{-PCF}_3)]$  **5**,  $[\text{Ru}_4(\text{CO})_{12}(\mu\text{-H})_2(\mu_3\text{-AsCF}_3)_2]$  **6**,  $[\text{Ru}_4(\text{CO})_{13}(\mu\text{-H})_2(\mu_4\text{-AsCF}_3)]$  **7**,  $[\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-AsCF}_3)_2]$  **8** and  $[\text{Ru}_5(\text{CO})_{15}(\mu\text{-H})_2(\mu_3\text{-AsCF}_3)_3]$  **9**. The structures **2** and **7** contain spiked ruthenium frameworks with a phosphinidene or arsinidene group co-ordinated to all four metal atoms. The molecular structures of **4** and **9** have been shown to contain two-metal and three-metal fragments joined together by three  $\mu_3$ -phosphinidene (or arsinidene) units. The hydrides in **2** and **7** display similar fluxional behaviour yielding the same values of  $\Delta G^\ddagger$  ( $= 49 \text{ kJ mol}^{-1}$ ). The transformation from **1** to **5**, probably *via* intermediate **2**, occurs with increase in nuclearity by the treatment of **1** with  $[\text{Ru}_3(\text{CO})_{12}]$ . Pathways for the formation of cluster **3** from **2**, **9** from  $[\text{Ru}_4(\text{CO})_{12}(\mu\text{-H})_2(\mu_3\text{-AsCF}_3)_2(\mu\text{-AsCF}_3)]$  **10**, and also **6** from **8** by hydrogenation are discussed.

## Introduction

Transition metal carbonyl cluster derivatives containing main group ligands have been a subject of considerable interest in recent years. A number of such clusters containing terminal, edge-bridged and capped phosphine ligands have been synthesized from the reactions of alkyl or aryl primary phosphines with appropriate carbonyl clusters. Thus, the reactions of  $[\text{M}_3(\text{CO})_{12}]$  ( $\text{M} = \text{Ru}$  or  $\text{Os}$ ) with  $\text{PRH}_2$  ( $\text{R} = \text{Ph}$ ,  $p\text{-MeOC}_6\text{H}_4$ , or  $p\text{-BrC}_6\text{H}_4$ ) under mild conditions were found to give a series of trinuclear derivatives, namely  $[\text{Os}_3(\text{CO})_{11}(\text{PPhH}_2)]$  with terminally bonded  $\text{PPhH}_2$ ,  $[\text{M}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-PPhH})]$  with bridging  $\text{PPhH}$  and  $[\text{M}_3(\text{CO})_9(\mu\text{-H})_2(\mu_3\text{-PR})]$  with capped  $\text{PR}$  ligands.<sup>1,2</sup> When the reactions were carried out under rigorous conditions clusters of higher nuclearity containing capped  $\text{PR}$  units were also obtained. It has been reported that the reactions between  $[\text{Ru}_3(\text{CO})_{12}]$  and  $\text{PPhH}_2$  in toluene under reflux conditions afford a range of products, comprising [in addition to the trinuclear cluster  $[\text{Ru}_3(\text{CO})_9(\mu\text{-H})_2(\mu_3\text{-PPh})]$  the square-planar cluster  $[\text{Ru}_4(\text{CO})_{11}(\mu\text{-H})(\mu_4\text{-PPh})_2]$ , square-pyramidal pentanuclear clusters  $[\text{Ru}_5(\text{CO})_{15}(\mu_4\text{-PPh})]$  and  $[\text{Ru}_5(\text{CO})_{13}(\mu\text{-H})(\mu_4\text{-PPh})\{\mu\text{-PPh}(\text{OP}^n)\}]$ , as well as the distorted trigonal-prismatic hexanuclear clusters  $[\text{Ru}_6(\text{CO})_{12}(\mu_4\text{-PPh})_2(\mu_3\text{-PPh})_2]$  and  $[\text{Ru}_6(\text{CO})_{12}(\mu_4\text{-PPh})_3(\mu_3\text{-PPh})]$ .<sup>3</sup> Compared to primary phosphines, little attention has been given to primary arsines. The reactions of  $\text{RAsH}_2$  ( $\text{R} = \text{aryl}$  group) with  $[\text{Ru}_3(\text{CO})_{12}]$  afford the bridged dinuclear derivatives  $[\text{Ru}_2(\text{CO})_6(\mu\text{-AsRH})_2]$  and capped trinuclear derivatives, namely  $[\text{Ru}_3(\text{CO})_9(\mu\text{-H})_2(\mu_3\text{-AsR})]$  and  $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-AsR})_2]$ .<sup>2</sup>

We now report a detailed investigation of the reactions of  $[\text{Ru}_3(\text{CO})_{12}]$  with the primary phosphine and arsine  $\text{CF}_3\text{EH}_2$  ( $\text{E} = \text{P}$  or  $\text{As}$ ) containing the highly electron-withdrawing  $\text{CF}_3$  group, whereupon some of the products isolated are different from those obtained from the analogous reactions with alkyl and aryl phosphines and arsines.

## Results and discussion

### Reactions and characterization

Reactions of  $\text{CF}_3\text{PH}_2$  with  $[\text{Ru}_3(\text{CO})_{12}]$  at elevated temperatures in  $\text{CH}_2\text{Cl}_2$  or  $p$ -xylene gave rise to a series of phosphinidene-capped clusters: a trinuclear cluster  $[\text{Ru}_3(\text{CO})_9(\mu\text{-H})_2(\mu_3\text{-PCF}_3)]$  **1**, spiked cluster  $[\text{Ru}_4(\text{CO})_{13}(\mu\text{-H})_2(\mu_4\text{-PCF}_3)]$  **2**, bent open chain cluster  $[\text{Ru}_4(\text{CO})_{12}(\mu\text{-H})_2(\mu_3\text{-PCF}_3)_2]$  **3** and two pentanuclear clusters  $[\text{Ru}_5(\text{CO})_{15}(\mu\text{-H})_2(\mu_3\text{-PCF}_3)_3]$  **4** and  $[\text{Ru}_5(\text{CO})_{15}(\mu_4\text{-PCF}_3)]$  **5**. From the reaction at  $80^\circ\text{C}$  **1** was isolated as a major product in relatively high yield. When the reaction temperature was raised to  $120^\circ\text{C}$  clusters **2** and **3** were formed in moderate yields, together with a very small amount of **4**. Higher temperatures favoured the formation of **3** and **5** and the reaction at  $170^\circ\text{C}$  gave **3** and **5** in moderate yields. However, clusters **1** and **5** have been earlier reported to be the products from the reactions of  $(\text{CF}_3\text{P})_4$  with  $[\text{Ru}_4(\text{CO})_{12}\text{H}_4]$  and  $[\text{Ru}_3(\text{CO})_{12}]$  respectively.<sup>4</sup>

The reactions of  $\text{CF}_3\text{AsH}_2$  with  $[\text{Ru}_3(\text{CO})_{12}]$  under the same conditions as for  $\text{CF}_3\text{PH}_2$  were found to yield similar products containing arsinidene ligands. These products are the open chain cluster  $[\text{Ru}_4(\text{CO})_{12}(\mu\text{-H})_2(\mu_3\text{-AsCF}_3)_2]$  **6**, the spiked cluster  $[\text{Ru}_4(\text{CO})_{13}(\mu\text{-H})_2(\mu_4\text{-AsCF}_3)]$  **7** as well as the pentanuclear cluster  $[\text{Ru}_5(\text{CO})_{15}(\mu\text{-H})_2(\mu_3\text{-AsCF}_3)_3]$  **9**. Cluster **7** has been obtained previously from the reaction of  $(\text{CF}_3\text{As})_4$  with  $[\text{Ru}_3(\text{CO})_{12}]$ .<sup>5</sup> These compounds are isostructural to their corresponding phosphorus analogues whose molecular structures have been determined by X-ray diffraction studies. Unlike the reactions where  $\text{CF}_3\text{PH}_2$  was used, the corresponding trinuclear cluster  $[\text{Ru}_3(\text{CO})_9(\mu\text{-H})_2(\mu_3\text{-AsCF}_3)]$  and pentanuclear cluster  $[\text{Ru}_5(\text{CO})_{15}(\mu_4\text{-AsCF}_3)]$  were not obtained.

The IR and NMR data of all the cluster derivatives we have synthesized are given in Table 1. The carbonyl stretching vibrations fall in the region between  $1900$  and  $2200 \text{ cm}^{-1}$  indicating that all carbonyl groups are terminal. These values reflect

**Table 1** Infrared spectroscopic<sup>a</sup> and NMR<sup>b</sup> data ( $\delta$ , J/Hz) for the complexes

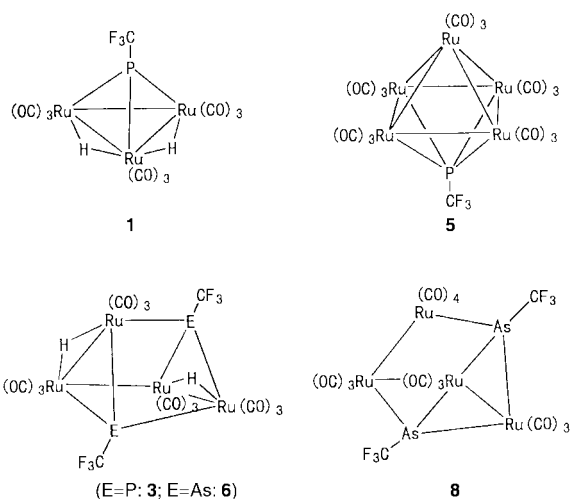
Complex	IR/ $\text{cm}^{-1}$	$^1\text{H}$	$^{31}\text{P}\{-^1\text{H}\}$	$^{19}\text{F}$
2	2104m, 2076s, 2058s, 2050m, 2032w, 2018w, 2009w, 1989w	-18.52 (s)	108 (q), $J(\text{PF}) = 51$	14.9 (d), $J(\text{PF}) = 51$
3	2101m, 2083m, 2063s, 2053w, 2037w, 2024m, 2006w	-13.92 (t), $J(\text{PH}) = 12$	-0.8 (m)	22.5 (m)
4	2105s, 2094m, 2082w, 2063w, 2051w, 2041w, 2017w, 1986w	-13.62 (t), $J(\text{PH}) = 16$ , -14.17 (dt), $J(\text{PH})_1 = 16$ , $J(\text{PH})_2 = 7^c$	40 (p), $J(\text{PF}) = 38$ , 87 (q), $J(\text{PF}) = 31$	28.9 (d), $J(\text{PF}) = 39$ , 25.0 (d), $J(\text{PF}) = 29$
6	2096m, 2081s, 2060s, 2049w, 2022m, 2003w	-13.35 (s)		30.0 (s)
7	2120w, 2101m, 2075s, 2055s, 2046m, 2031w, 2015w, 1990w	-18.60 (s)		19.8 (s)
9	2102s, 2089s, 2080w, 2060m, 2047m, 2041m, 2017w, 1981w	-13.95 (s), -14.74 (s)		33.8 (s), 27.3 (s)

<sup>a</sup> Recorded in hexane. <sup>b</sup> Recorded in  $\text{CDCl}_3$ . <sup>c</sup> The subscripts 1 and 2 refer to coupling between P and the near (1) and far (2) bridging protons.

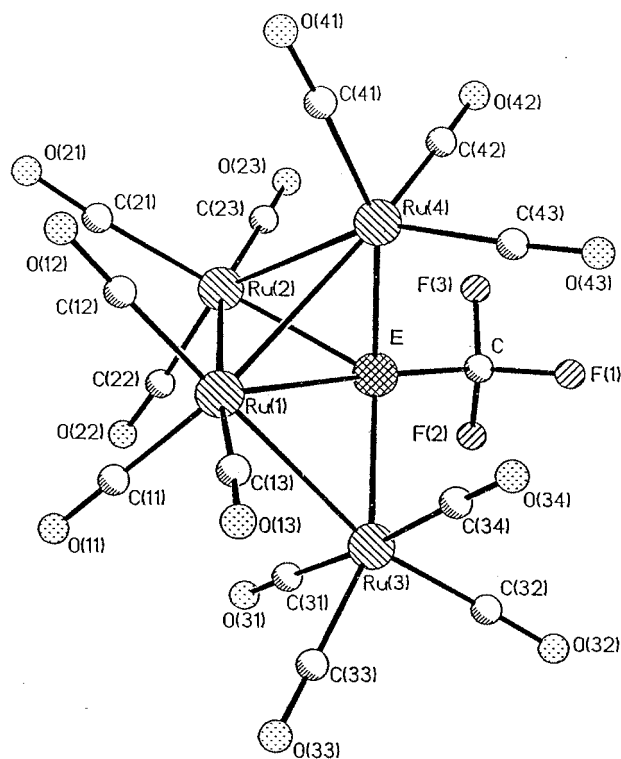
an increase of about  $100\text{ cm}^{-1}$  compared to those of other ruthenium compounds containing non-fluorinated phosphine and arsine ligands. The IR spectra also showed C–F stretching vibrations at around  $1100\text{--}1200\text{ cm}^{-1}$ , typical of trifluoromethylated phosphine compounds. However, the C–F deformation modes were not observed due to low intensity. It can be observed from Table 1 that complexes **2**, **3** and **4** show very high-field signals in their  $^{31}\text{P}$  NMR spectra compared to other ruthenium carbonyl clusters containing  $\mu_3$ - and  $\mu_4$ -phosphinidene ligands.<sup>6</sup>

### Structures of compounds **3** and **6**

The proposed structural formula of compound **6** (based on spectroscopic data) is shown below. In the attempted X-ray analysis of this cluster the low diffracting power of crystals obtained and the resulting low number of observed reflections allowed only the heavy atoms to be refined anisotropically and some bond lengths associated with the light atoms had to be fixed at ideal values. In addition, the broadening of the reflection peaks indicates high disorder of the crystal resulting in poor data. Thus, identification of the heavy atom (Ru, As) positions in an incompletely refined X-ray analysis shows that the four ruthenium atoms in cluster **6** adopt a linear configuration with the two arsinidene groups capping at the 1,2,4 and 1,3,4 positions. To date a few clusters of the same structural type are known, e.g. clusters  $[\text{Ru}_4(\text{CO})_{12}(\mu\text{-H})_2(\mu_3\text{-PPh})_2]$ <sup>7</sup> and  $[\text{Os}_4(\text{CO})_{12}(\mu\text{-H})_2(\mu_3\text{-E})]$ <sup>8</sup> where E = S or Se. However, **6** is the first example for the arsinidene clusters.



The structures of clusters **3** and **6** have been found to be similar on the basis of their IR, NMR and microanalytical data. In **3** the two bridging hydrides give a virtual triplet in the  $^1\text{H}$  NMR spectrum with an average  $J(\text{PH})$  coupling of approximately 12 Hz. These hydrides are chemically but not



**Fig. 1** Molecular structures of compounds **2** (E = P) and **7** (E = As).

magnetically equivalent. Its  $^{31}\text{P}\{-^1\text{H}\}$  and  $^{19}\text{F}$  NMR spectra show an approximate  $X_3AA'X'_3$  pattern,<sup>9–11</sup> reflecting a weak coupling between the two phosphorus atoms. The  $^{31}\text{P}\{-^1\text{H}\}$  NMR resonance of **3** appears at  $\delta -0.8$ , which is very unusual for  $\mu_3$ -phosphinidene ligands in ruthenium carbonyl clusters.<sup>6</sup> The  $^{19}\text{F}$  NMR spectrum of **6** exhibits a singlet at  $\delta 30.0$  indicating the existence of two equivalent  $\text{CF}_3$  groups. Its  $^1\text{H}$  NMR spectrum shows a singlet at  $\delta -13.35$ , consistent with the presence of two equivalent hydrides.

### Crystal structures of compounds **2** and **7**

The crystal structure of compound **2**, as illustrated in Fig. 1, reveals a spiked  $\text{Ru}_4$  core with only a  $\mu_4$ -phosphinidene ligand which is co-ordinated with every metal atom. However, the phosphinidene does not bond equally strongly with the four metal atoms. The longest Ru–P bond distance observed is  $\text{Ru}(1)\text{--P}$  [ $2.759(3)\text{ \AA}$ ] (Table 2), which is shorter than the  $2.779\text{ \AA}$  in  $[\text{Ru}_3(\text{CO})_6(\mu\text{-H})(\mu\text{-PPh})]$ <sup>12</sup> and  $2.864(2)\text{ \AA}$  in  $[\text{Ru}_4(\text{CO})_{14}(\mu_4\text{-PCF}_3)]$ .<sup>4</sup> The Ru–Ru bond distances vary over a wide range, from  $2.838(1)$  to  $3.013(1)\text{ \AA}$ , and the longest bond length is displayed by  $\text{Ru}(1)\text{--Ru}(4)$ . One question in **2** concerns the location of the two hydride ligands. The  $^1\text{H}$  NMR spectra at low temperatures (see Fig. 3) show no coupling between these two hydrides, indicating that they are not co-ordinated to

**Table 2** Selected bond lengths (Å) and bond angles (°) for the complexes **2**, **4**, **7** and **9**

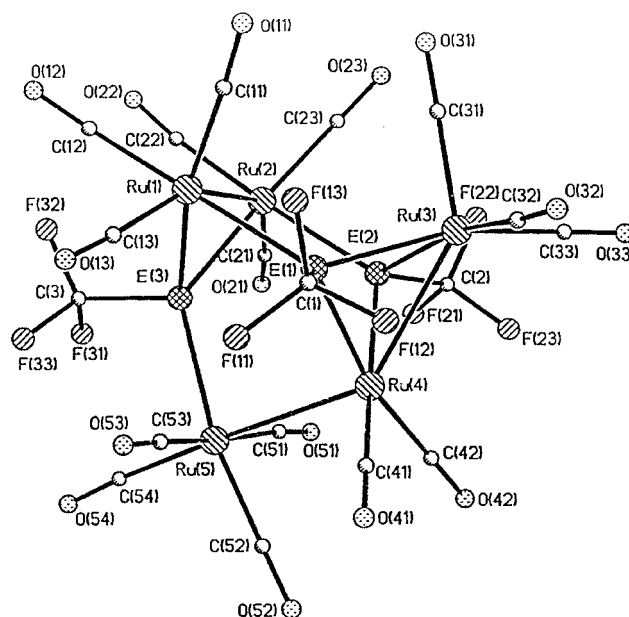
<b>2</b>			
Ru(1)–Ru(2)	2.838(1)	Ru(1)–P	2.759(3)
Ru(2)–Ru(4)	2.900(1)	Ru(2)–P	2.331(3)
Ru(1)–Ru(3)	2.920(1)	Ru(3)–P	2.394(3)
Ru(1)–Ru(4)	3.013(1)	Ru(4)–P	2.359(3)
Ru(1)–Ru(2)–Ru(4)	63.34(4)	Ru(2)–Ru(4)–Ru(1)	57.33(4)
Ru(2)–Ru(1)–Ru(3)	92.00(5)	Ru(4)–Ru(1)–Ru(2)	59.33(4)
Ru(4)–Ru(1)–Ru(3)	88.27(4)		
<b>7</b>			
Ru(1)–Ru(2)	3.0310(3)	Ru(1)–As	2.8568(4)
Ru(1)–Ru(3)	2.9588(4)	Ru(2)–As	2.4540(4)
Ru(1)–Ru(4)	2.8684(4)	Ru(3)–As	2.4751(4)
Ru(2)–Ru(4)	2.9233(3)	Ru(4)–As	2.4245(4)
Ru(1)–Ru(2)–Ru(4)	57.563(8)	Ru(2)–Ru(1)–Ru(3)	90.473(9)
Ru(2)–Ru(4)–Ru(1)	63.105(8)	Ru(4)–Ru(1)–Ru(2)	59.332(8)
Ru(4)–Ru(1)–Ru(3)	93.221(10)		
<b>4</b>			
Ru(1)–Ru(2)	2.992(2)	Ru(3)–P(1)	2.394(2)
Ru(3)–Ru(4)	2.875(2)	Ru(3)–P(2)	2.400(2)
Ru(4)–Ru(5)	2.849(2)	Ru(4)–P(1)	2.375(2)
Ru(1)–P(1)	2.437(2)	Ru(4)–P(2)	2.382(2)
Ru(1)–P(3)	2.405(2)	Ru(5)–P(3)	2.456(2)
Ru(2)–P(2)	2.442(2)		
Ru(2)–P(3)	2.392(2)	Ru(3)–Ru(4)–Ru(5)	139.0(1)
<b>9</b>			
Ru(1)–Ru(2)	3.035(2)	Ru(3)–As(1)	2.480(3)
Ru(3)–Ru(4)	2.925(2)	Ru(3)–As(2)	2.489(2)
Ru(4)–Ru(5)	2.854(2)	Ru(4)–As(1)	2.472(2)
Ru(1)–As(1)	2.526(2)	Ru(4)–As(2)	2.475(2)
Ru(1)–As(3)	2.489(2)	Ru(5)–As(3)	2.542(2)
Ru(2)–As(2)	2.530(2)		
Ru(2)–As(3)	2.476(2)	Ru(3)–Ru(4)–Ru(5)	140.10(6)

adjacent Ru–Ru bonds. For this reason we tentatively assign the  $\mu$ -H atoms to the two bridging locations which span the spiked Ru(1)–Ru(3) bond and the Ru(2)–Ru(4) bond in the ruthenium triangle.

The structure of arsenic cluster **7** closely resembles that of **2**. It also consists of a triangular array of Ru atoms with another Ru atom bound to one of the axial co-ordination sites of Ru(1) on the ruthenium triangle. The average Ru–Ru bond length in **7** is in the normal range but somewhat larger than that of **2**, showing a little cluster expansion (2.945 *vis.* 2.918 Å). The tetrametal spiked geometry of **2** and **7** is an alternative metal arrangement to the butterfly geometry observed in  $[\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-PPh})]^{13}$  and  $[\text{Ru}_4(\text{CO})_{13}\text{H}_2(\mu_3\text{-PPh})]^{14}$  for the 64-electron system.

### Crystal structures of compounds **4** and **9**

The molecular structure of compound **4** is given in Fig. 2. It contains an open deltahedral fragment Ru(3)–Ru(4)–Ru(5) and a dimetal fragment Ru(1)–Ru(2) which are approximately perpendicular to each other and joined by three phosphinidene groups. Both P(1) and P(2) bridge Ru(3) and Ru(4) nearly symmetrically and are co-ordinated to Ru(1) and Ru(2) respectively. The bridging hydrides were not located directly, but the spectroscopic and structural data are consistent with them bridging the Ru(1)–Ru(2) and Ru(3)–Ru(4) edges. For this cluster as well as **9**, further supportive evidence for the location of the bridging hydrides can be derived from the comparatively large Ru(4)–Ru(3)–C(33) [111.3(2), **4**; 109.9(5)°, **9**] and Ru(3)–Ru(4)–C(42) [113.8(2), **4**; 112.7(5)°, **9**] angles. The Ru–P distances [average 2.401(2) Å] fall within the range of the normal Ru–P bond distances. Carbon–oxygen distances are all reasonable, ranging from 1.117(10) to 1.151(10) Å, and the Ru–C–O



**Fig. 2** Molecular structures of compounds **4** (E = P) and **9** (E = As).

systems are all close to linear, with angles ranging from 173.7(8) to 179.8(7)°.

The molecular structure of arsenic cluster **9** is very similar to that of **4**. It also contains an open trinuclear chain and a dinuclear unit of Ru atoms held together by three  $\mu_3$ -arsinidene groups. The Ru–As bond lengths lie within the range 2.472(2)–2.542(2) Å with a slightly larger Ru–As bond associated with Ru(5). The average Ru–Ru bond length is *ca.* 0.03 Å longer than the average distance of 2.905 Å in **4**. To our knowledge, the skeletal stereochemistry of **4** and **9** is unprecedented for a pentanuclear cluster.

In the high-field range of the  $^1\text{H}$  NMR spectrum of compound **4** two sets of signals are observed. One is a triplet at  $\delta$  –13.62, due to coupling with the two phosphinidene ligands, and assigned to the hydride bridging the Ru(3)–Ru(4) bond. The other is a doublet of triplets at  $\delta$  –14.17 as a result of coupling with the three phosphinidene ligands and thus can be assigned to the hydride bridging the Ru(1)–Ru(2) edge. Its  $^{31}\text{P}$  NMR spectrum shows two signals at  $\delta$  40 and 87 with an integration ratio of 2:1, representing the three  $\mu_3$ -PCF<sub>3</sub> bridging units of which two are nearly equivalent. The  $^{19}\text{F}$  NMR spectrum of **9** exhibits two singlets at  $\delta$  33.8 and 27.3 with the intensity ratio 2:1, as expected for the solid state structure. Its  $^1\text{H}$  NMR spectrum displays two singlets at  $\delta$  –13.95 and –14.74 with the intensity ratio 1:1 indicating the presence of two structurally non-equivalent hydrides.

### Hydride fluxional behaviour of compounds **2** and **7**

The proton coupled  $^{31}\text{P}$  NMR spectrum of compound **2** shows a triplet of quartets at  $\delta$  108.4 with a  $J(\text{PH})$  coupling constant of 15.4 Hz, suggesting the presence of two hydrides in the cluster. However, only a very broad strongly shielded resonance at  $\delta$  –18.5 is observed in the  $^1\text{H}$  NMR spectrum at room temperature owing to rapid exchange of the hydrides between the metal–metal edges on the NMR timescale. When the temperature is lowered, as illustrated in Fig. 3, the singlet broadens further to a huge hump which coalesces at about –3 °C and finally separates into two doublets at  $\delta$  –16.80 [ $J(\text{PH})$  = 16.03] and –20.20 [ $J(\text{PH})$  = 15.05 Hz] with an integration ratio of 1:1. When the temperature is returned to room temperature only a singlet is observed at the original position indicating that there is no decomposition of **2** during the variable temperature studies. The energy barrier for this fluxional behavior is estimated to be 49 kJ mol<sup>–1</sup> by the coalescence temperature method. This is slightly higher than that of  $[\text{Ru}_4(\text{CO})_{12}(\mu\text{-H})_3]$

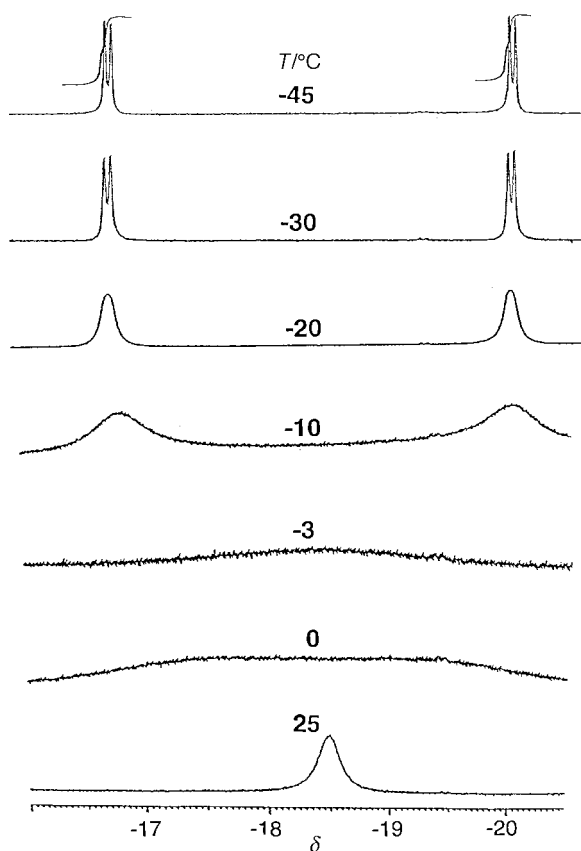


Fig. 3 VT-<sup>1</sup>H NMR Spectra of compound 2.

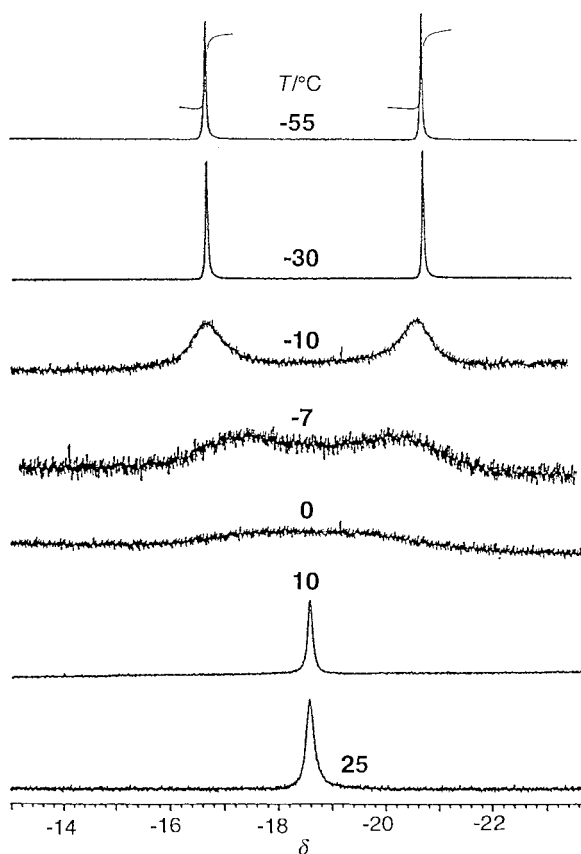


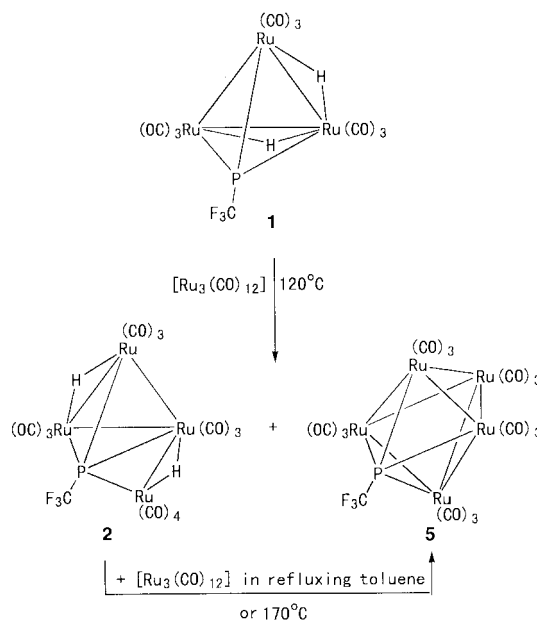
Fig. 4 VT-<sup>1</sup>H NMR Spectra of compound 7.

$\{\mu\text{-P}(\text{CF}_3)_2\}$ <sup>15</sup> and those reported in other tetraruthenium clusters where  $\Delta G^\ddagger$  varies from 31 to 38 kJ mol<sup>-1</sup>.<sup>16,17</sup> The fluxional behavior of the two hydrides in 7 is similar to that of its

phosphorus analogue 2. At room temperature, the high-field region of the <sup>1</sup>H NMR spectrum of 7 shows only one singlet at  $\delta$  -18.60, a consequence of the hydride fluxionality. This singlet is nearly completely lost at the coalescence temperature of 0 °C. As the temperature is further decreased two broadened signals emerge and the spectrum at -55 °C displays two singlets with the same intensity at  $\delta$  -16.61 and -20.64 (See Fig. 4). The activation energy is also estimated to be 49 kJ mol<sup>-1</sup>.

### Reactivity studies

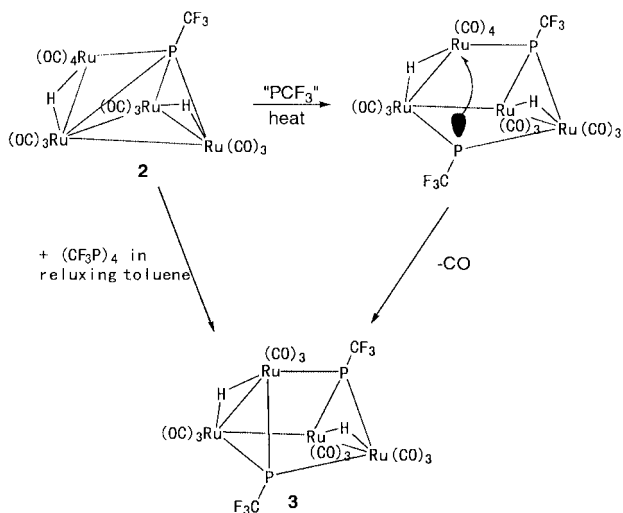
The spiked cluster 2 can be regarded as an “axially metallo-ligated” triangular cluster. This observation prompted us to study the relationship between 2 and trinuclear cluster 1. We found that the reaction of 1 with [Ru<sub>3</sub>(CO)<sub>12</sub>] in refluxing toluene yielded a greenish solid mixture. The IR and <sup>31</sup>P-<sup>1</sup>H NMR spectra of this solid showed that it contained a mixture of cluster 2 and the pentanuclear cluster 5 in an approximate 2:1 ratio. The relative yield of 2 and 5 is not markedly affected by the reaction conditions. The increase in nuclearity from cluster 1 to 2 and 5 implies that the reaction may involve the successive addition of a “Ru(CO)<sub>n</sub>” ( $n = 4$  or 3) fragment to 1. Treatment of 2 with [Ru<sub>3</sub>(CO)<sub>12</sub>] in refluxing toluene results in the conversion of 2 into 5 in 90% yield, which indicates that the formation of 5 from 1 occurs possibly *via* the intermediacy of 2 (Scheme 1). Similar reactions of [M<sub>3</sub>(CO)<sub>12</sub>] (M = Ru or Os)



Scheme 1 The reaction of compound 1 with [Ru<sub>3</sub>(CO)<sub>12</sub>] and the conversion of 2 into 5.

with trinuclear cluster [Os<sub>3</sub>(CO)<sub>9</sub>( $\mu$ -H)<sub>2</sub>( $\mu_3$ -PPh)] at elevated temperatures were reported previously,<sup>18</sup> where, instead of spiked clusters like 2, butterfly clusters with the general formula [MO<sub>3</sub>(CO)<sub>12</sub>( $\mu$ -H)<sub>2</sub>( $\mu_3$ -PR)] were obtained.

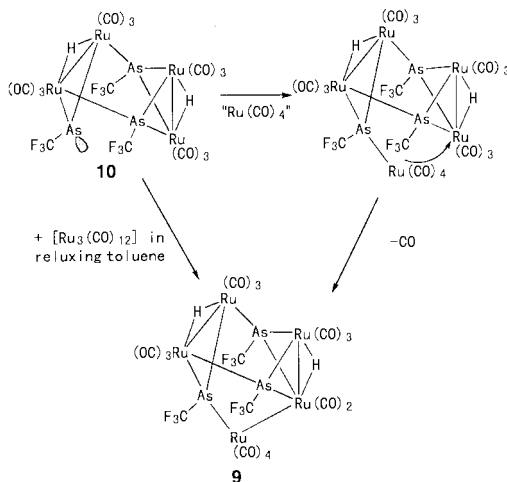
Careful examination of the structures of compounds 2 and 3 reveals that addition of the four-electron donor “PCF<sub>3</sub>” to the spiked cluster 2 would probably cause a Ru–Ru bond to break along with the dissociation of a CO ligand leading to the formation of 3, where the skeletal Ru atoms assume an open chain structure. Indeed, heating 2 at 110 °C for a day with cyclophosphine (PCF<sub>3</sub>)<sub>4</sub> [a source of PCF<sub>3</sub> fragments] in toluene leads to the conversion of 2 into 3 in about 52% yield. A possible pathway for this conversion based on metal–metal bond cleavage is given in Scheme 2. Accordingly, the initial step for the formation of 3 may involve the breaking of a Ru–Ru bond in 2 providing a vacant site for the incoming “PCF<sub>3</sub>” unit. The next step, CO substitution by the phosphorus lone pair, occurs



Scheme 2 Proposed pathway for the conversion of compound 2 into 3.

to form cluster 3. The addition of donor ligands such as phosphines leading to the breaking of a metal–metal bond has also been demonstrated by the interconversions among clusters  $[\text{Fe}_2\text{Mn Cp}(\text{CO})_8(\text{PPh})]$ ,  $[\text{Fe}_2\text{Mn Cp}(\text{CO})_9(\text{PPh})]$  and  $[\text{Fe}_2\text{Mn Cp}(\text{CO})_{10}(\text{PPh})]$  where metal–metal bonds are broken by the addition of CO or phosphine ligands and reformed by CO removal without change in their structures.<sup>19</sup>

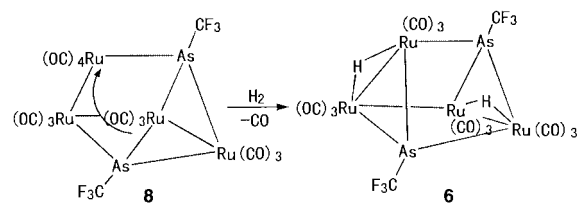
Arsenic cluster 9 can also be obtained from arsenic cluster 10 [earlier reported from the reaction of  $(\text{AsCF}_3)_4$  with  $[\text{Ru}_4(\text{CO})_{12}\text{H}_4]$ ] by reaction in refluxing toluene with  $[\text{Ru}_3(\text{CO})_{12}]$ , which gives a yield of 83%. The formation of 9, as illustrated in Scheme 3, probably proceeds *via* co-ordination of the arsenic



Scheme 3 Proposed pathway for the conversion of compound 10 into 9.

atom to the “ $\text{Ru}(\text{CO})_4$ ” fragment [derived from thermal fragmentation of the parent  $[\text{Ru}_3(\text{CO})_{12}]$ ]. This is followed by coupling of a metal–metal bond together with the elimination of a carbon monoxide molecule. Such transformation of 10 to 9 [which bears a close structural relationship] could conceivably have occurred in the reaction of  $\text{CF}_3\text{AsH}_2$  with  $[\text{Ru}_3(\text{CO})_{12}]$  where 9 is also isolated.

The hydrogenation of compound 8 by passing hydrogen in refluxing octane for 30 min gave 6 in a quantitative yield. The conversion of 8 into 6 can be understood in terms of the skeletal rearrangement as illustrated in Scheme 4. The shift of a Ru–As bond from Ru(2) to Ru(3) and the addition of two hydrides affords arsenic cluster 6, which assumes a prismatic structure, where the bridging hydrides are located at the two triangular planes.



Scheme 4 The hydrogenation of compound 8.

## Conclusion

The reactions of primary trifluoromethyl-phosphine and -arsine  $\text{CF}_3\text{EH}_2$  ( $\text{E} = \text{P}$  or  $\text{As}$ ) with  $[\text{Ru}_3(\text{CO})_{12}]$  occur with cleavage of two E–H bonds to form a series of phosphinidene- and arsinidene-capped clusters 1–9. Unlike derivatives 1, 3, 5 and 8, which are structurally similar to those obtained with the alkyl and aryl primary phosphines and arsines, the spiked ruthenium clusters 2 and 7 and open chain clusters 4 and 9 are structurally new and have hitherto not been synthesized from the analogous reactions with the alkyl and aryl ligands. Of the seven clusters which contain bridging hydrides, only spiked 2 and 7 display fluxional behaviour, yielding the same values of  $\Delta G^\ddagger$  ( $=49 \text{ kJ mol}^{-1}$ ). The structural relationships of several new clusters are demonstrated by the following transformation reactions: (a) 1 can be transformed to 2 and 5 successively by the addition of a “ $\text{Ru}(\text{CO})_4$ ” fragment, followed by elimination of CO ligands; (b) pentanuclear 9 is derived from the structurally related tetranuclear 10, also by the addition of a “ $\text{Ru}(\text{CO})_4$ ” fragment, as illustrated in Scheme 3; (c) incorporation of the  $\text{CF}_3\text{P}$  group into 2 gives the prismatic structure 3; and (d) hydrogenation of 8 occurs without structural change to form 6, resulting in shift of the Ru–As bond from Ru(2) to Ru(3) together with loss of a CO ligand.

## Experimental

### General comments

As  $\text{CF}_3\text{EH}_2$  ( $\text{E} = \text{P}$  or  $\text{As}$ ) compounds are air sensitive and highly toxic, their syntheses and handling were carried out using all-glass vacuum lines equipped with Teflon gas-tight taps. All the reactions were performed in vacuum using reaction vessels equipped with Teflon taps or in sealed glass tubes. The solvents were distilled prior to use under a nitrogen atmosphere over the appropriate drying agent. Products were separated by TLC using laboratory-prepared  $20 \times 20 \text{ cm}$  glass plates coated to 0.3 mm thickness with Merck Kieselgel 60F<sub>254</sub> silica gel. The IR spectra were recorded on a Perkin-Elmer 983G or 1600 FT-IR spectrometer, NMR spectra on either a Bruker ACF-300 or JEOL FX-90Q FT spectrometer. Compounds  $[\text{Ru}_3(\text{CO})_{12}]$ ,<sup>20</sup>  $\text{CF}_3\text{EH}_2$  ( $\text{E} = \text{P}$  or  $\text{As}$ )<sup>21</sup> and  $(\text{CF}_3\text{P})_4$ ,<sup>22</sup> were prepared by literature methods.

Crystal data and details of measurement for compounds 2, 4, 7, and 9 are given in Table 3. Diffraction intensities were collected at 298 K on a Siemens R3m/V (for 4), a Rigaku AFC5R (for 2 and 9) and a Smart CCD diffractometer (for 7). The structures were solved by direct methods and the refinement was by the full-matrix, least-squares method with all non-hydrogen atoms refined anisotropically except for 2, where the atoms of CO ligands were refined isotropically. All computations were carried out using either a SHELXTL PLUS (PC version)<sup>23</sup> or a MolEN program package.<sup>24</sup>

CCDC reference number 186/1555.

See <http://www.rsc.org/suppdata/dt/1999/2799/> for crystallographic files in .cif format.

### Reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with $\text{CF}_3\text{PH}_2$

(a) At 80 °C. The compound  $\text{CF}_3\text{PH}_2$  (32 mg, 0.31 mmol) was condensed into a degassed solution of  $[\text{Ru}_3(\text{CO})_{12}]$  (200 mg,

**Table 3** Crystallographic data for complexes **2**, **4**, **7** and **9**

	<b>2</b>	<b>4</b>	<b>7</b>	<b>9</b>
Formula	C <sub>14</sub> H <sub>2</sub> F <sub>3</sub> O <sub>13</sub> PRu <sub>4</sub>	C <sub>18</sub> H <sub>2</sub> F <sub>9</sub> O <sub>15</sub> P <sub>3</sub> Ru <sub>5</sub>	C <sub>14</sub> H <sub>2</sub> AsF <sub>3</sub> O <sub>13</sub> Ru <sub>4</sub>	C <sub>18</sub> H <sub>2</sub> As <sub>3</sub> F <sub>9</sub> O <sub>15</sub> Ru <sub>5</sub>
Formula weight	870.28	1227.4	914.36	1359.29
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>Pbca</i>	<i>P2<sub>1</sub>/n</i>	<i>Pbca</i>	<i>P2<sub>1</sub>/n</i>
<i>a</i> /Å	16.541(4)	9.948(2)	17.3431(2)	9.972(6)
<i>b</i> /Å	18.287(3)	17.690(8)	15.46710(10)	17.810(6)
<i>c</i> /Å	15.901(3)	18.649(8)	18.0049(2)	18.891(7)
$\beta$ /°		96.27(3)		95.64(4)
<i>V</i> /Å <sup>3</sup>	4809.6(3)	3262(2)	4829.77(8)	3339.0(4)
<i>Z</i>	8	4	8	4
$\mu$ /cm <sup>-1</sup>	12.80	25.24	38.96	52.3
Number of reflections measured	4719	5987	29612	6460
Number of independent reflections	4719	5662	6243	6085
Number of reflections used in refinement	2746 [ $F_o > 3\sigma(F)$ ]	4097 [ $F_o > 4\sigma(F)$ ]	6243 [ $I > 2\sigma(I)$ ]	3895 [ $F_o > 3\sigma(F)$ ]
<i>R</i>	0.051	0.0313	0.0252	0.060
<i>R</i> '	0.060	0.0364	0.0448	0.074

0.31 mmol) in 10 ml of *p*-xylene at liquid-nitrogen temperature. The reaction mixture was allowed to warm to room temperature and then heated with stirring in CH<sub>2</sub>Cl<sub>2</sub> at 80 °C for 18 h. The resulting dark green solution was evaporated to dryness. The residue was dissolved in the minimum volume of CH<sub>2</sub>Cl<sub>2</sub> and separated by TLC using hexane as eluent to give a yellow band ( $R_f = 0.80$ ) of complex **1** (89 mg, 44%) (Found: C, 18.33; H, 0.21; F, 8.09; P, 4.67. C<sub>10</sub>H<sub>2</sub>F<sub>3</sub>O<sub>9</sub>PRu<sub>3</sub> requires C, 18.26; H, 0.30; F, 8.67; P, 4.72%). A very small amount of **2** ( $R_f = 0.53$ ) was also isolated from this reaction (11 mg, 5%) (Found: C, 19.18; H, 0.21; F, 7.02; P, 3.56. C<sub>14</sub>H<sub>2</sub>F<sub>3</sub>O<sub>13</sub>PRu<sub>4</sub> requires C, 19.30; H, 0.23; F, 6.55; P, 3.56%).

(b) At 120 °C. The compound CF<sub>3</sub>PH<sub>2</sub> (32 mg, 0.31 mmol) was condensed into a degassed solution of [Ru<sub>3</sub>(CO)<sub>12</sub>] (200 mg, 0.31 mmol) in 10 ml of *p*-xylene. The mixture was heated in a sealed tube at 120 °C for 18 h. After removing the solvent under vacuum, the brown residue was taken up in the minimum volume of CH<sub>2</sub>Cl<sub>2</sub> and separated by TLC using hexane as eluent to give yellow bands of **1** ( $R_f = 0.81$ ) (26 mg, 13%), **2** ( $R_f = 0.47$ ) (61 mg, 30%), **3** ( $R_f = 0.60$ ) (32 mg, 15%) (Found: C, 18.13; P, 6.72. C<sub>7</sub>HF<sub>3</sub>O<sub>6</sub>PRu<sub>2</sub> requires C, 17.83; P, 6.58%), and **4** ( $R_f = 0.16$ ) (8 mg, 4%) (Found: C, 17.55; F, 13.74; P, 7.64. C<sub>18</sub>H<sub>2</sub>F<sub>9</sub>O<sub>15</sub>P<sub>3</sub>Ru<sub>5</sub> requires C, 17.60; F, 13.93; P, 7.58%).

(c) At 170 °C. The reaction conditions were similar to those described in (b). Clusters **3** ( $R_f = 0.51$ ; 16 mg, 7%) and **5** ( $R_f = 0.43$ ; 43 mg, 22%) (Found: C, 18.71; F, 5.92; P, 2.99. C<sub>16</sub>F<sub>3</sub>O<sub>15</sub>PRu<sub>5</sub> requires C, 18.73; F, 5.56; P, 3.02%) were obtained after TLC.

#### Reaction of [Ru<sub>3</sub>(CO)<sub>12</sub>] with CF<sub>3</sub>AsH<sub>2</sub>

(a) At 80 °C. The reaction is analogous to that of (a) above except that CF<sub>3</sub>AsH<sub>2</sub> was used instead of CF<sub>3</sub>PH<sub>2</sub>. The CF<sub>3</sub>AsH<sub>2</sub> (45.24 mg, 0.31 mmol) was treated with [Ru<sub>3</sub>(CO)<sub>12</sub>] (200 mg, 0.31 mmol). Four complexes were obtained from this reaction after TLC separation using hexane as eluent; they are **6** ( $R_f = 0.55$ ; 20 mg, 8%) (Found: C, 16.35; H, 0.17; As, 14.98. C<sub>7</sub>HAsF<sub>3</sub>O<sub>6</sub>Ru<sub>2</sub> requires C, 16.31; H, 0.19; As, 14.55%), **7** ( $R_f = 0.47$ ; 48 mg, 23%) (Found: C, 18.29; As, 8.16. C<sub>14</sub>H<sub>2</sub>-AsF<sub>3</sub>O<sub>13</sub>Ru<sub>4</sub> requires C, 18.38; As, 8.20%), **8** ( $R_f = 0.37$ ; 12 mg, 5%) (Found: C, 17.19; As, 13.71; F, 11.30. C<sub>15</sub>As<sub>2</sub>F<sub>6</sub>O<sub>13</sub>Ru<sub>4</sub> requires C, 17.04; As, 14.19; F, 10.79%), and **9** ( $R_f = 0.20$ ; 10 mg, 4%) (Found: C, 15.85; F, 12.74. C<sub>18</sub>H<sub>2</sub>As<sub>3</sub>F<sub>9</sub>O<sub>15</sub>Ru<sub>5</sub> requires C, 15.89; F, 12.58%).

(b) At 120 °C. The reaction was similar to (b) above except that CF<sub>3</sub>AsH<sub>2</sub> was used instead of CF<sub>3</sub>PH<sub>2</sub>. The CF<sub>3</sub>AsH<sub>2</sub> (45.24 mg, 0.31 mmol) was treated with [Ru<sub>3</sub>(CO)<sub>12</sub>] (200 mg,

0.31 mmol). Complexes **6** ( $R_f = 0.53$ ; 27 mg, 11%), **7** ( $R_f = 0.45$ ; 35 mg, 16%), **8** ( $R_f = 0.31$ ; 10 mg, 4%), and **9** ( $R_f = 0.14$ ; 21 mg, 8%) were obtained after TLC using hexane as eluent.

#### Reaction of compound **1** with [Ru<sub>3</sub>(CO)<sub>12</sub>]

Compound **1** (35 mg, 0.053 mmol) and [Ru<sub>3</sub>(CO)<sub>12</sub>] (34 mg, 0.0053 mmol) were placed in a single reaction vessel with 8 ml toluene and degassed. The reaction mixture was stirred for 24 h at 120 °C, and the solvent evaporated. Purification by preparative TLC (hexane as eluent) afforded **2** and **5** (28 mg).

#### Reaction of compound **2** with [Ru<sub>3</sub>(CO)<sub>12</sub>]

A toluene solution (5 ml) of compound **2** (20 mg, 0.023 mmol) and [Ru<sub>3</sub>(CO)<sub>12</sub>] (15 mg, 0.023 mmol) was heated at reflux for 21 h. The residue was purified by preparative TLC (hexane as eluent) to afford **5** ( $R_f = 0.46$ ; 17 mg, 90%).

#### Thermolysis of compound **2**

Compound **2** (70 mg, 0.08 mmol) and 5 ml of degassed *p*-xylene were sealed in a glass ampoule and heated to 170 °C for 18 h. The green solution was evaporated to dryness *in vacuo* and separated by TLC using hexane as eluent to give **5** ( $R_f = 0.41$ ; 25 mg, 38%).

#### Reaction of compound **2** with (CF<sub>3</sub>P)<sub>4</sub>

Cluster **2** (60 mg, 0.069 mmol) was degassed with 8 ml of toluene and then (CF<sub>3</sub>P)<sub>4</sub> (14 mg, 0.035 mmol) introduced at liquid-nitrogen temperature. The mixture was allowed to react at 110 °C for 18 h. At the end of the reaction the solvent was removed *in vacuo* and the residue extracted with CH<sub>2</sub>Cl<sub>2</sub> and subjected to TLC using hexane as eluent. From the second band ( $R_f = 0.46$ ), **3**, identified *via* IR data, was isolated (34 mg, 52% yield based on **2**).

#### Reaction of compound **10** with [Ru<sub>3</sub>(CO)<sub>12</sub>]

Compounds **10** (30 mg, 0.026 mmol) and [Ru<sub>3</sub>(CO)<sub>12</sub>] (20 mg, 0.031 mmol) were degassed with 5 ml of toluene. The reaction mixture was heated to reflux for 18 h. The residue was purified by preparative TLC using hexane as eluent to give **9** ( $R_f = 0.15$ ; 23 mg, 83%).

#### Hydrogenation of compound **8**

Compound **8** (96 mg, 0.091 mmol) was suspended in 60 ml of octane in a two-necked round-bottomed flask equipped with a hydrogen inlet tube, a reflux condenser and a magnetic stirrer. The solution was then heated at 120 °C for 30 min with continuous purging with hydrogen (1 atm). Removal of solvent and

recrystallization using CH<sub>2</sub>Cl<sub>2</sub>-hexane yielded orange crystals of **6** (86 mg, 92%).

## Acknowledgements

We thank the National University of Singapore for financial support and for Research Scholarships (to S. Du and B. H. Sow).

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Paper 9/02598G