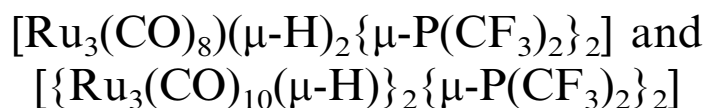


The reactions of bis(trifluoromethyl) phosphine and arsine with trinuclear ruthenium carbonyl cluster: molecular structures of the trinuclear and double-linked trinuclear clusters



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Received 20 April 1999; received in revised form 23 June 1999

Abstract

Reactions of $(\text{CF}_3)_2\text{EH}$ ($\text{E} = \text{P}, \text{As}$) with $[\text{Ru}_3(\text{CO})_{12}]$ under varying conditions result in hydrogen transfer from ligand to cluster to form trinuclear cluster $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2\{\mu\text{-P}(\text{CF}_3)_2\}_2]$ **1**, double-linked trinuclear clusters $[\{\text{Ru}_3(\text{CO})_{10}(\mu\text{-H})\}_2\{\mu\text{-E}(\text{CF}_3)_2\}_2]$ (**2**: $\text{E} = \text{P}$; **3**: $\text{E} = \text{As}$), flat butterfly cluster $[\text{Ru}_4(\text{CO})_{13}\{\mu\text{-P}(\text{CF}_3)_2\}_2]$ **4**, butterfly clusters $[\text{Ru}_4(\text{CO})_{12}(\mu\text{-H})_3\{\mu\text{-E}(\text{CF}_3)_2\}_2]$ (**5**: $\text{E} = \text{P}$; **6**: $\text{E} = \text{As}$), open-chain clusters $[\text{Ru}_4(\text{CO})_{14}\{\mu\text{-E}(\text{CF}_3)_2\}_2]$ (**7**: $\text{E} = \text{P}$; **8**: $\text{E} = \text{As}$) and square pyramidal clusters $[\text{Ru}_5(\text{CO})_{15}(\mu_4\text{-ECF}_3)]$ (**9**: $\text{E} = \text{P}$; **10**: $\text{E} = \text{As}$). Cluster **1** contains a triangular Ru plane with two short Ru–Ru bonds bridged by a phosphido and a hydride, respectively. Cluster **2** consists of two coplanar Ru_3 triangles linked by two phosphido groups. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cluster; Phosphido; Arsinido; Double linked; Molecular structure

1. Introduction

Earlier studies of the reactions of primary and secondary trifluoromethyl-substituted phosphines with metal carbonyl complexes have shown that in most reactions, the products are usually simple substitution derivatives. With iron and cobalt carbonyls, cleavage of the P–H bond has occurred to form phosphido bridged dinuclear complexes such as $[\text{Fe}_2(\text{NO})_4\{\text{P}(\text{CF}_3)_2\}_2]$, $[\text{Co}_2(\text{CO})_6\{\text{P}(\text{CF}_3)_2\}_2]$ and $[\text{H}_2\text{Fe}_2(\text{CO})_6\{\mu\text{-P}(\text{CF}_3)_2\}_2]$ [1–5]. By comparison, few studies have been undertaken on reactions of $(\text{CF}_3)_2\text{AsH}$ with metal complexes. It has been reported that the reaction with $[\text{MnCo}(\text{CO})_9]$ gave $[(\text{CO})_5\text{Mn}\{(\text{CF}_3)_2\text{As}\}]$ complex [6]. We wish to report the reactions of $(\text{CF}_3)_2\text{EH}$ ($\text{E} = \text{P}, \text{As}$) with $[\text{Ru}_3(\text{CO})_{12}]$, which have given rise to a wide range of cluster derivatives that have been isolated and characterized.

2. Results and discussion

2.1. Reactions and characterization

As shown in Table 1, the reaction of equimolar amounts of $(\text{CF}_3)_2\text{PH}$ with $[\text{Ru}_3(\text{CO})_{12}]$ at 80°C in dichloromethane for 18 h gave a red solution. Removal of solvent and other volatile compounds followed by TLC using hexane as eluant gave clusters $[\text{Ru}_4(\text{CO})_{13}\{\mu\text{-P}(\text{CF}_3)_2\}_2]$ **4**, $[\text{Ru}_4(\text{CO})_{12}(\mu\text{-H})_3\{\mu\text{-P}(\text{CF}_3)_2\}_2]$ **5** and $[\{\text{Ru}_3(\text{CO})_{10}(\mu\text{-H})\}_2\{\mu\text{-P}(\text{CF}_3)_2\}_2]$ **2**. Further, via a similar reaction with a two-fold molar amount of the ligand, in addition to cluster **4**, another two new clusters $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2\{\mu\text{-P}(\text{CF}_3)_2\}_2]$ **1** and $[\text{Ru}_4(\text{CO})_{14}\{\mu\text{-P}(\text{CF}_3)_2\}_2]$ **7** were also isolated. However, in a similar reaction using equimolar amounts of reactants at a higher temperature of 110°C , cluster **4** and a pentanuclear cluster $[\text{Ru}_5(\text{CO})_{15}(\mu_4\text{-PCF}_3)]$ **9** were obtained; at the much higher temperature of 180°C overnight, a dark green solution was obtained, which affords two

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Table 1
Summary of the reactions of (CF₃)₂PH with [Ru₃(CO)₁₂]

Conditions	Products	R _f ^a	Yields (%)
CH ₂ Cl ₂ , 80°C, 18 h, 1:1	[{Ru ₃ (CO) ₁₀ (μ-H) ₂ {μ-P(CF ₃) ₂ } ₂] 2	0.22	3
	[Ru ₄ (CO) ₁₃ {μ-P(CF ₃) ₂ } ₂] 4	0.43	6
	[Ru ₄ (CO) ₁₂ (μ-H) ₃ {μ-P(CF ₃) ₂ }] 5	0.32	20
CH ₂ Cl ₂ , 80°C, 18 h, 1:2 (ligand)	[Ru ₃ (CO) ₈ (μ-H) ₂ {μ-P(CF ₃) ₂ } ₂] 1	0.61	4
	[Ru ₄ (CO) ₁₃ {μ-P(CF ₃) ₂ } ₂] 4	0.56	7
	[Ru ₄ (CO) ₁₄ {μ-P(CF ₃) ₂ } ₂] 6	0.21	8
<i>p</i> -Xylene, 110°C (or 180°C), 18 h, 1:1	[Ru ₄ (CO) ₁₃ {μ-P(CF ₃) ₂ } ₂] 4	0.50 (0.49)	5 (3)
	[Ru ₅ (CO) ₁₅ (μ ₄ -PCF ₃)] 7	0.38 (0.40)	6 (17)

^a Hexane as eluant.

major products: cluster **4** and a green crystal identified to be cluster **9**.

As shown in Table 2, the reaction of [Ru₃(CO)₁₂] with an equal molar amount of (CF₃)₂AsH at 80°C overnight gave a red residue upon removal of solvent. Separation of the products by TLC using hexane as eluant gave [Ru₄(CO)₁₂(μ-H)₃{μ-As(CF₃)₂}] **6**, [{Ru₃(CO)₁₀(μ-H)₂{μ-As(CF₃)₂}₂] **3** and [Ru₄(CO)₁₄{μ-As(CF₃)₂}₂] **8**. In a similar reaction using 1:2 molar ratio of the reactants, the products remain the same but with slightly different yields. Under more rigorous conditions at higher temperatures of 130°C, clusters **6** and **8** were obtained. The reaction at 170°C gave a pentanuclear arsenidine cluster [Ru₅(CO)₁₅(μ₄-AsCF₃)] **10** as the major product.

Clusters **3–10** are not new. Clusters **3–5** have been previously isolated from the reactions of (CF₃)₂PP(CF₃)₂ with [Ru₃(CO)₁₂] and [H₄Ru₄(CO)₁₂] [7], cluster **7** from the reaction of (PCF₃)₄ with [Ru₃(CO)₁₂] [8], and clusters **6**, **8** and **10** from the reactions of [Ru₃(CO)₁₂] with (CF₃)₂AsGeH₃, (CF₃)₂AsN₃ and CF₃As(N₃)₂ respectively [9]. A diagram of the molecular structures of these cluster derivatives is illustrated in Fig. 1. The X-ray crystal structure determinations of **1** and **2** were carried out.

The spectroscopic data for the new cluster derivatives **1–3** are given in Table 3. The IR spectra of clusters **2** and **3** have a similar absorption pattern, indicating their structural similarity. The hydride ligands in clusters **1–3**

Table 2
Summary of the reactions of (CF₃)₂AsH with [Ru₃(CO)₁₂]

Conditions	Products	R _f	Yields (%)
CH ₂ Cl ₂ , 80°C, 18h, 1:1	[{Ru ₃ (CO) ₁₀ (μ-H) ₂ {μ-As(CF ₃) ₂ } ₂] 3	0.35 ^a	3
	[Ru ₄ (CO) ₁₂ (μ-H) ₃ {μ-As(CF ₃) ₂ }] 8	0.47	8
	[Ru ₄ (CO) ₁₄ {μ-As(CF ₃) ₂ } ₂] 9	0.25	27
CH ₂ Cl ₂ , 80°C, 18h, 1:2 (ligand)	[{Ru ₃ (CO) ₁₀ (μ-H) ₂ {μ-As(CF ₃) ₂ } ₂] 3	0.22 ^a	3
	[Ru ₄ (CO) ₁₂ (μ-H) ₃ {μ-As(CF ₃) ₂ }] 8	0.45	6
	[Ru ₄ (CO) ₁₄ {μ-As(CF ₃) ₂ } ₂] 9	0.18	13
<i>p</i> -Xylene, 130°C, 18h, 1:1	[Ru ₄ (CO) ₁₂ (μ-H) ₃ {μ-As(CF ₃) ₂ }] 8	0.47 ^b	5
	[Ru ₄ (CO) ₁₄ {μ-As(CF ₃) ₂ } ₂] 9	0.24	14
<i>p</i> -Xylene, 170°C, 18h, 1:1	[Ru ₅ (CO) ₁₅ (μ ₄ -AsCF ₃)] 10	0.53 ^b	4

^a Pentane as eluant.

^b Hexane as eluant.

Table 3
IR and NMR data for clusters **1**, **2** and **3**

Cluster	IR ν(CO) (cm ⁻¹)	¹ H	³¹ P{ ¹ H}	¹⁹ F
1	2108w, 2078vs, 2047s, 2040m, sh 2028w	–18.43(t)	177.4(m)	27.5(m) 21.6(m)
2	2109m, 2085w, 2065m, 2054s, 2037w	–18.00(t)	71.3(m)	27.6(d)
3	2107m, 2083w, 2067w, 2051s, 2035m	–18.41(s)		26.53(s)

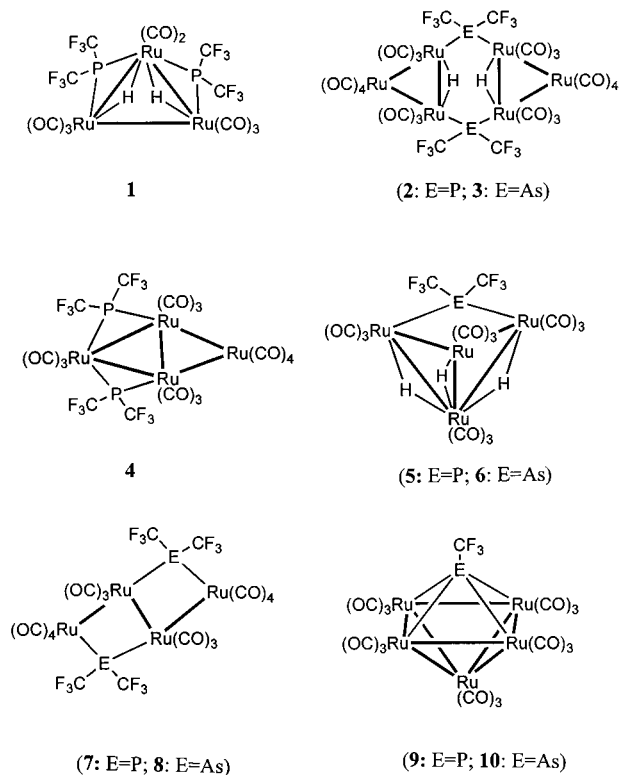
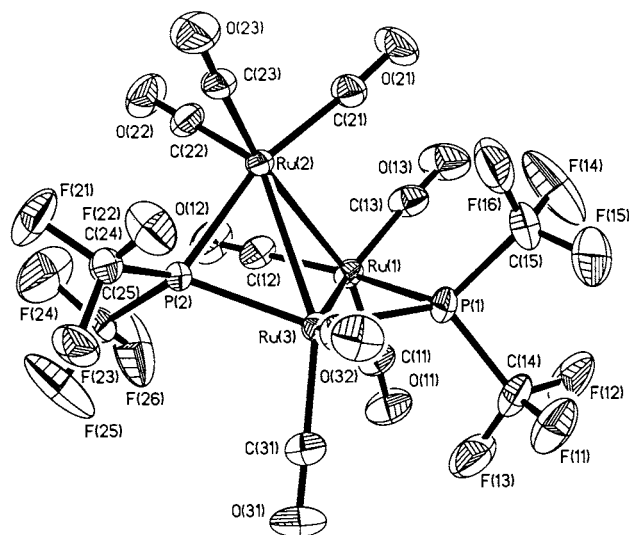


Fig. 1. Molecular structures of the cluster derivatives.

resonate at about $\delta - 18$, a common observation for hydrides bridging an Ru_3 triangle. The downfield position of the $^{31}\text{P}\{^1\text{H}\}$ -NMR signal in **1** (δ 177.4) is consistent with these phosphido groups bridging metal atoms joined by a metal–metal bond [10]. The highfield shift of the $^{31}\text{P}\{^1\text{H}\}$ -NMR signal of **2** (δ 71.3) is characteristic of the phosphido ligands bridging metal atoms without a metal–metal bond [10].

2.2. Molecular structure of **1**

Cluster **1** crystallizes in the triclinic space group $P\bar{1}$ with two molecules per symmetry unit. The molecular structure is shown in Fig. 2, and the selected bond lengths and angles are listed in Table 4. Cluster **1** consists of a closed 48-electron Ru_3 cluster in which two short Ru–Ru bonds are bridged by $\mu\text{-P}(\text{CF}_3)_2$ units [Ru(2)–Ru(3) = 2.877(1) Å and Ru(1)–Ru(3) = 2.877(1) Å]. The phosphido groups lie on opposite sides of the trimetal plane with the dihedral angles between the Ru(1)Ru(2)Ru(3) plane and the Ru(1)Ru(3)P(1) and the Ru(2)Ru(3)P(2) planes being 116.4 and 62.5°, respectively. The structure is similar to those of the diphenylphosphido and di-*tert*-butylphosphido analogues. The unique Ru(3), which is bonded to two phosphido groups, also bears two *cis*-CO ligands. The other two ruthenium atoms each have three CO groups and are separated by a fairly long Ru–Ru bond of

Fig. 2. Molecular structure of cluster **1**.

2.960(1) Å. Although the two hydrides are not located directly from the X-ray structure, it is reasonable to assume that they occupy the bridging sites across Ru(1)–Ru(3) and Ru(2)–Ru(3), opposite to the $\mu\text{-P}(\text{CF}_3)_2$ groups. Thus, the phosphido groups are roughly *trans* to each other with P(1)–Ru(3)–P(2) being 140.2(1)°, which is a little smaller than that in $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2\{\mu\text{-P}(\text{Bu}'_2)\}_2]$ [151.6(5)°] [11]. The fact that the two hydride ligands bridge short Ru–Ru bonds reveals that metal bond lengthening by the hydride ligand is largely offset by the shortening effect of the bridging phosphido groups. The Ru–Ru distances in **1** are, on average, shorter than those in $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2\{\mu\text{-P}(\text{Bu}'_2)\}_2]$ [11] [2.905(1) vs. 2.956(1) Å]. On the other hand, the average Ru–P distance of **1** is 2.314(1) Å which is 0.061 Å shorter than the average distance of 2.388(1) Å in cluster $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2\{\mu\text{-P}(\text{Bu}'_2)\}_2]$ [11]. Such comparison can be extended to other structurally related trinuclear species containing diphenylphosphido ligands. This shortening is due to the highly electronegative CF_3 groups, which tend to increase the positive charge on the P atom and therefore increase the bond strength.

2.3. Molecular structure of **2**

The molecular structure of **2** is illustrated in Fig. 3 and the important bond lengths and angles are given in Table 4. In the structure of **2**, two discrete Ru_3 triangles are linked via two phosphido groups. The six metal atoms are coplanar with two phosphorus atoms being above and below this plane by 0.207 Å, giving a rare example of a six-membered ring of four ruthenium and two phosphorus atoms. The molecular structure of **2** possesses a symmetry centre that overlaps the crystallographic symmetry centre. Such a structure has not been

Table 4
Selected bond lengths (Å) and angles (°) of clusters **1** and **2**

Cluster 1	Ru(1)–Ru(2)	2.960(1)	Ru(3)–P(1)	2.295(1)
	Ru(1)–Ru(3)	2.877(1)	Ru(2)–P(2)	2.331(1)
	Ru(2)–Ru(3)	2.877(1)	Ru(3)–P(2)	2.291(1)
	Ru(1)–P(1)	2.340(1)		
	Ru(1)–Ru(2)–Ru(3)	59.0(1)	Ru(1)–P(1)–Ru(3)	76.7(1)
	Ru(1)–Ru(3)–Ru(2)	61.9(1)	Ru(2)–P(2)–Ru(3)	77.0(1)
	Ru(2)–Ru(1)–Ru(3)	59.0(1)	P(1)–Ru(3)–P(2)	140.2(1)
Cluster 2	Ru(1)–Ru(2)	3.047(1)	Ru(1)–P(1)	2.388(2)
	Ru(1)–Ru(3)	2.878(1)	Ru(2)–P(1a)	2.388(2)
	Ru(2)–Ru(3)	2.884(1)		
	Ru(1)–Ru(2)–Ru(3)	58.0(1)	Ru(1)–P(1)–Ru(2a)	126.5(1)
	Ru(1)–Ru(3)–Ru(2)	63.8(1)	Ru(2)–Ru(1)–Ru(3)	58.2(1)

reported before for ruthenium carbonyl clusters and its skeletal stereochemistry is most unusual. As in other linked trimetal clusters reported, the two metal triangles are joined by only one phosphido or phosphinidene group with a dihedral angle between them, ranging from 25.5 to 88.8°. Furthermore, the structure of **2** also differs from other structures of phosphorus-bridged clusters in the orientation of the two metal triangles. It has been found that the dihedral angles between the metal planes, as well as their relative orientation with respect to each other, vary considerably in the linked trimetal clusters such as $[\text{Os}_6(\mu\text{-H})(\text{CO})_{22-n}\text{L}_n(\mu\text{-PH}_2)]$ ($n = 0$ or 1 ; $\text{L} = \text{CO}$, phosphine, nitrile or isocyanide) [12].

In the Ru(1)–Ru(2)–Ru(3) triangle of **2**, the Ru(1)–Ru(2) bond is the longest edge. The metal hydride, though not located crystallographically, most probably bridges these two ruthenium atoms, since it has been shown that the presence of a $\mu\text{-H}$ bridge on a ruthenium triangle causes lengthening of the bridged Ru–Ru bond compared with the other two Ru–Ru distances [13]. The lengthening effect is

further enhanced by the coordination of the phosphido ligands to Ru(1) and Ru(2). These findings are consistent with the observation that the substitution of a CO group by a σ -donating ligand at the equatorial position usually results in the lengthening of the M–M bond *cis* to it [14]. On the other hand, it is usually found in carbonyl compounds that also contain phosphines and bridging ligands that, as far as possible, the hydride ligands bridge the most electron-rich metal–metal bonds that are *cis* to the phosphorus atoms, even though these metal–metal bonds are the more sterically hindered bonds [15]. According to this observation, the two hydrides are most likely to bridge across Ru(1)–Ru(2) and Ru(1A)–Ru(2A), respectively.

It is worth noting that a wide Ru–P–Ru angle [$126.5(1)^\circ$] is observed for **2**, which is slightly larger than that [$119.5(1)^\circ$] in **7** but significantly greater than that [$110.9(1)^\circ$] of **4**. Among the many phosphido-bridged transition metal complexes that have been synthesized in recent years are a relatively small number of compounds in which the phosphido ligands bridge non-bonding metal–metal edges. In fact, for ruthenium carbonyl clusters containing non-fluorinated phosphido ligands, the only example is the open triruthenium cluster $[\text{Ru}_3(\text{CO})_9(\text{C}_2\text{Pr-}i)(\mu\text{-PPh}_2)]$ [16], where the diphenyl-phosphido ligand bridges an open Ru–Ru bond with a Ru–P–Ru angle of $92.8(1)^\circ$, which is much smaller than $126.5(1)^\circ$ in **2**. By comparison with large M–P–M angles for some transition metal phosphido compounds where metal–metal bonding is absent, it is apparent that cluster **2** displays very large M–P–M angles. In addition, clusters of the types **2**, **4** and **7** involving big Ru–P–Ru angles have not been isolated from the reactions using non-fluorinated phosphines.

The initial step in the formation of cluster **2** probably involves the substitution reaction of an axial carbonyl

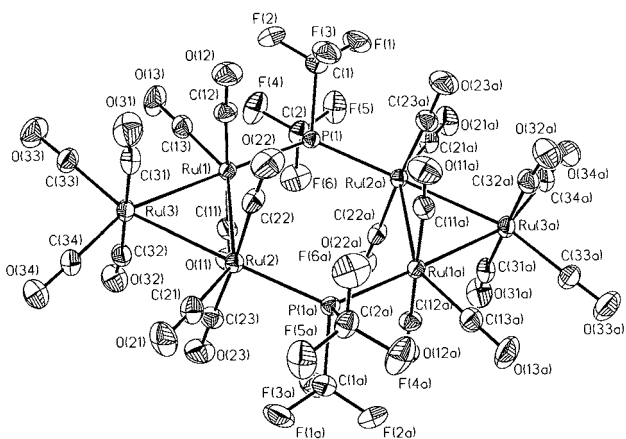
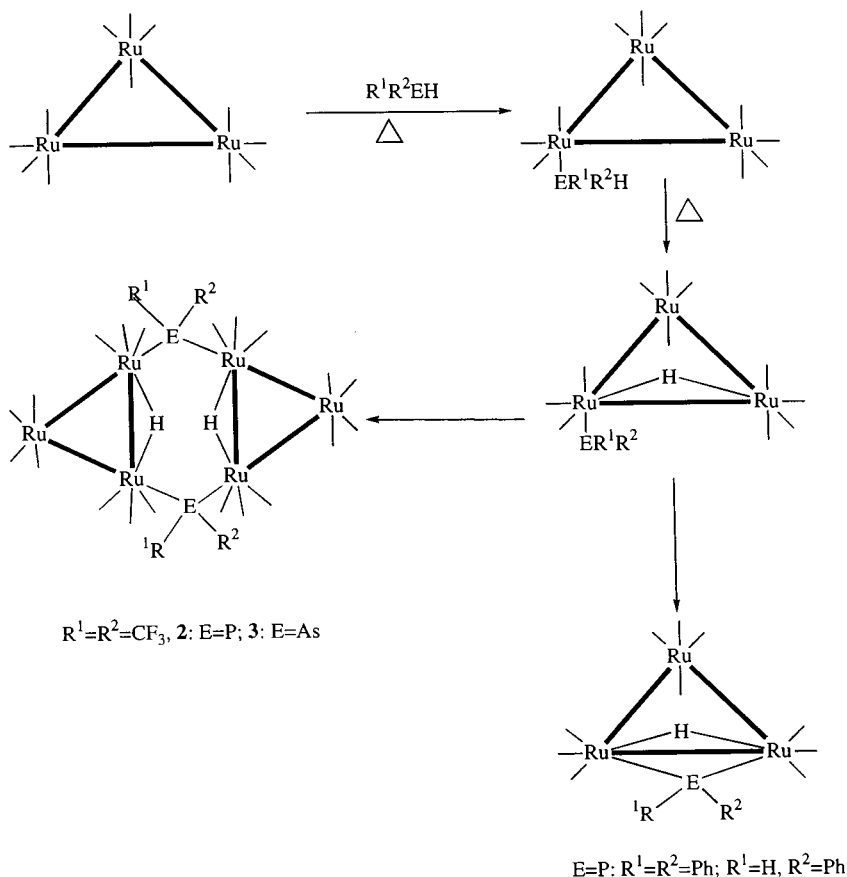


Fig. 3. Molecular structure of cluster **2**.



Scheme 1. Proposed pathways for 2.

group by $P(CF_3)_2H$ ligand to give the terminally bound phosphine intermediate $[Ru_3(CO)_{11}\{P(CF_3)_2H\}]$. This is followed by hydrogen migration from phosphine to a Ru–Ru edge to form intermediate $[Ru_3(CO)_{11}(\mu-H)\{P(CF_3)_2\}]$, which interacts with another molecule of $[Ru_3(CO)_{11}(\mu-H)\{P(CF_3)_2\}]$ to form linked cluster 2. However, the reaction we have obtained is different from that reported with primary and secondary phenylphosphine, where the CF_3 -phosphido group bridges two Ru_3 rings intermolecularly whereas the Ph-phosphido group forms a bridge on one Ru_3 ring in an intramolecular manner, as shown in Scheme 1 [13,17].

3. Experimental

3.1. General comments

All manipulations were performed in vacuo and all solvents were distilled from appropriate drying agents. IR spectra were recorded in hexane solutions on a Perkin–Elmer FT-IR 2000 spectrophotometer. NMR spectra were obtained on a ACF Bruker 300 MHz spectrometer. The complexes $[Ru_3(CO)_{12}]$ [18] and

$(CF_3)_2EH$ (E = P, As) [19] were synthesized according to the literature methods.

3.2. Reactions of $(CF_3)_2PH$ with $[Ru_3(CO)_{12}]$

The reactions are summarized in Table 1. In a typical reaction, $[Ru_3(CO)_{12}]$ (200 mg, 0.31 mmol) and 10 ml of CH_2Cl_2 were placed in a double reaction vessel, and degassed with four freeze–pump–thaw cycles. Then $(CF_3)_2PH$ (52.7 mg, 0.31 mmol) was condensed in. The reaction mixture was heated at 80°C for 18 h. The solvent was removed on the vacuum line and the remaining solid was chromatographed by TLC using hexane as eluant to give cluster derivatives 4, 5, and 2. Elemental analysis of 2 gave C 19.15 (Anal. Calc. C 19.12%).

Similarly, the reaction using two-fold amount of ligand at 80°C afforded cluster derivatives 1, 4 and 7. Elemental analysis of 1 gave C 16.84 (Anal. Calc. C 16.60%).

3.3. Reactions of $(CF_3)_2AsH$ with $[Ru_3(CO)_{12}]$

The reactions are summarized in Table 2. In a typical reaction, $[Ru_3(CO)_{12}]$ (200 mg, 0.31 mmol) was placed

Table 5
Crystal data and refinement details for **1** and **2**

Cluster	1	2
Empirical formula	C ₁₂ H ₂ O ₈ F ₁₂ P ₂ Ru ₃	C ₂₄ H ₂ F ₁₂ O ₂₀ P ₂ Ru ₆
Formula weight	867.21	1506.42
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	8.292(2)	11.152(4)
<i>b</i> (Å)	17.535(3)	16.203(4)
<i>c</i> (Å)	18.287(3)	11.357(4)
α (°)	112.145(9)	90
β (°)	96.966(9)	97.43(3)
γ (°)	90.468(16)	90
<i>U</i>	2440(2)	2034.8(12)
<i>Z</i>	4	2
<i>D</i> (g cm ⁻³)	2.355	3.032
μ	20.91	24.91
Temperature	23	23
Scan mode	ω	ω
Scan speed (°/min in ω)	2.00 to 29.30	3.00 to 16.74
Scan range	0.60	1.20
Max. 2θ	45	50
Number of data collected	15637	3790
Number of indept. data	11142	3599
Number of observ. data	9303 [$F_o > 4\sigma(F)$]	2891 [$F_o > 4\sigma(F)$]
Number of parameters	668	290
<i>R</i>	0.0396	0.0296
<i>R_w</i>	0.0620	0.0355
Goodness-of-fit	0.86	1.32
Largest diff. peak (e Å ⁻³)	1.09	0.54
Lowest diff. peak (e Å ⁻³)	-0.94	-0.41

in a double reaction vessel with 10 ml CH₂Cl₂ and degassed. (CF₃)₂AsH (66.3 mg, 0.31 mmol) was condensed and the mixture was stirred at 80°C for 18 h. The solvent was removed in vacuo and the residue was chromatographed by TLC using pentane as eluant to give cluster derivatives **3**, **6** and **8**.

3.4. X-ray structure determination

Crystal data and details of measurement for compounds **1** and **2** are given in Table 5. Diffraction intensities were collected at 298 K on a SMART CCD (for **1**) and Siemens R3m/V (for **2**) X-ray diffractometers with graphite-monochromatised Mo-K α radiation ($\lambda = 0.71073$ Å). All computations were carried out using the SHELXTL PLUS (PC version) program package [20]. The structures were solved by direct methods. Refinement was performed by the full-matrix, least-squares method with all non-hydrogen atoms being refined anisotropically.

Acknowledgements

We thank the National University of Singapore for financial support. S.D. is grateful to the University for the award of research scholarships.

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