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Journal of Organometallic Chemistry 589 (1999) 133–137

Reactions of spiked and open chain cluster hydrides with Au complexes: skeletal rearrangement and crystal structures of heterometallic clusters $[Au_2Ru_4(CO)_{12}(\mu_4\text{-}PCF_3)(PMe_3)_2]$ and $[Au_2Ru_4(CO)_{12}(\mu_3\text{-}PCF_3)_2(PPh_3)_2]$

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

Abstract

Treatment of the spiked cluster $[Ru_4(CO)_{13}(\mu\text{-}H)_2(\mu_4\text{-}PCF_3)]$ with $[Au(PMe_3)Cl]$ in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) results in deprotonation and metal core rearrangement from spiked to butterfly, yielding the heterometallic cluster $[Au_2Ru_4(CO)_{12}(\mu_4\text{-}PCF_3)(PMe_3)_2]$ **1**. Reaction of the open chain cluster $[Ru_4(CO)_{12}(\mu\text{-}H)_2(\mu_3\text{-}PCF_3)_2]$ with $[Au(PPh_3)Cl]$ under similar conditions gives $[Au_2Ru_4(CO)_{12}(\mu_3\text{-}PCF_3)_2(PPh_3)_2]$ **2** where the hydrides are simply replaced by $AuPPh_3$ fragments. Clusters **1** and **2** are characterised by spectroscopy and X-ray crystallography. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Heterometallic cluster; Molecular structure; Spiked; Open Chain

1. Introduction

Over the last decade, there have been numerous reports of heterometallic clusters containing one or more $AuPR_3$ groups together with other transition metals [1]. Such compounds are commonly prepared by the reaction of metal hydrido carbonyl clusters or their anions with R_3PAuX ($X = Cl$, Br, PF_6, etc; R = alkyl or aryl), usually by the simple substitution of hydrides by the $AuPR_3$ fragments. However, very few such reactions involving cluster hydrides ligated by main group elements have been reported. One example is the reaction between $[Ru_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}S)]$ and $[AuMe(PPh_3)]$, which affords two mixed-metal clusters, $[AuRu_3(CO)_8(\mu\text{-}H)(\mu_3\text{-}S)(PPh_3)L]$ and $[Au_2Ru_3(CO)_8(\mu_3\text{-}S)(PPh_3)L]$ (L = CO or PPh_3) in which the ruthenium triangle remains intact [2]. On the other hand, the cluster anion $[Ru_3(CO)_{12}(\mu\text{-}H)(\mu\text{-}PPh)]^-$ has been employed to react with $AuPR'_2R^+$ to give $[AuRu_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}PPh)(PR'_2R)]$ (R′ = R = Et; R′ = Me, R = Ph) in which further deprotonation of hydride was unsuccessful [3]. Herein, we report the reactions of the spiked cluster $[Ru_4(CO)_{13}(\mu\text{-}H)_2(\mu_4\text{-}PCF_3)]$ and the linear cluster $[Ru_4(CO)_{12}(\mu\text{-}H)_2(\mu_3\text{-}PCF_3)_2]$ with $AuPR_3^+$, resulting in metal skeletal rearrangement and the substitution of hydrides by $AuPR_3$ fragments occurred.

2. Results and discussion

2.1. Reactions and characterization

The reaction of the spiked cluster $[Ru_4(CO)_{13}(\mu\text{-}H)_2(\mu_4\text{-}PCF_3)]$ with a two-fold molar amount of $[Au(PMe_3)Cl]$ in dichloromethane at room temperature in the presence of DBU for 8 h gave a red–brown solution from which the heterometallic cluster $[Au_2Ru_4(CO)_{12}(\mu_4\text{-}PCF_3)(PMe_3)_2]$ **1** was isolated in 22% yield after chromatographic separation by TLC using a mixture of dichloromethane–hexane (v/v, 1:2) as eluant ($R_f = 0.37$) (Scheme 1). The CF_3 group is detected in the ^{19}F-NMR spectrum as a doublet at δ 17.66 with a $J_{P-F} = 61.06$ Hz. The ^1H-NMR spectrum gave two singlets at δ 1.67 and 1.64, which were assigned to the resonances of the two slightly inequivalent Me groups. Two singlets, broadened by quadrupolar effects from

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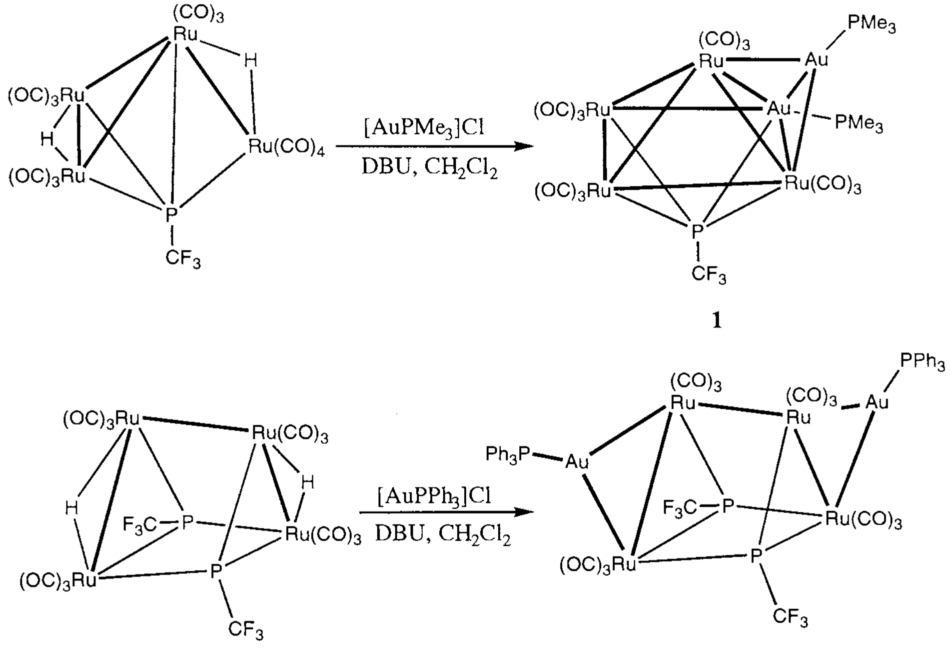
PII: S0022-328X(99)00369-1

the Au atoms, are observed in the ambient-temperature $^{31}P\{^1H\}$-NMR spectrum of **1**. The singlet at low field (δ 356.53) can be assigned to the μ_4-phosphinidene ligand whilst the other which appears at high field (δ 19.80) is due to the PMe_3 fragments. From the ground-state structure of **1**, it is clear that the two trimethylphosphine ligands are at distinct sites and should resonate with different chemical shifts. However, this high-field singlet remains unresolved even at −60°C.

Treatment of a dichloromethane solution of the mixture of $[Ru_4(CO)_{12}(\mu\text{-}H)_2(\mu_3\text{-}PCF_3)_2]$ and $[Au(PPh_3)Cl]$ with a three-fold molar amount of DBU at room temperature for 24 h afforded the cluster $[Au_2Ru_4(CO)_{12}(\mu_3\text{-}PCF_3)_2(PPh_3)_2]$ (**2**) (21% yield) after TLC separation using a mixture of dichloromethane–hexane (v/v, 1:2) as eluant ($R_f = 0.76$) (Scheme 1). The infrared spectrum of **2** in hexane gave ν(CO) absorption bands at 2102w, 2077m, 2057m, 2039s, 2021s and 1986w cm^{-1}. The ^1H-NMR spectrum showed a multiplet at δ 7.73–7.12 due to phenyl groups. The $^{31}P\{^1H\}$-NMR spectrum showed two broad multiplet signals at δ 66.16 and 56.04 in a 1:1 ratio. The ^{19}F-NMR spectrum consists of only one multiplet at δ 21.50 assigned to the phosphinidene groups.

The formation of cluster **1** clearly involves a skeletal rearrangement from spiked to butterfly as a result of the Ru(2) becoming detached from the cap μ_4-PCF_3 ligand to form a new Ru–Ru bond. The evidence on the formation of the dianion intermediate was based on the observation that after deprotonation $[Ru_4(CO)_{13}(\mu\text{-}H)_2(\mu_4\text{-}PCF_3)]$ with excess DBU, no hydride signal was detected in its ^1H-NMR spectrum. Such detachment of a bridging or capping phosphorus ligand is unusual but is not without precedent [4]. However, unlike other reactions, where the replacement of hydrides by MPR_3 moieties (M = Cu, Ag and Au) has little effect on the cluster core or overall geometry, the formation of **1** from $[Ru_4(CO)_{13}(\mu\text{-}H)_2(\mu_4\text{-}PCF_3)]$ involves ruthenium skeletal transformation from spiked to butterfly geometry. Moreover, the Ru_4Au_2 framework in **1** and **2** has no precedent in the literature, though a number of heteronuclear clusters exhibiting structures in which a Group IB metal caps a triangular face of a polyhedron containing transition metals and a second coinage metal are known. The most related clusters are $[H_2Ru_4(CO)_{12}\{Au(PPh_3)\}_2]$ [5,6] where the Ru atoms are arranged in a tetrahedral framework. Examples of other mixed-metal clusters containing a μ_4-PR ligand are rare. Typical examples are $[Fe_2Co_2(CO)_{11}(PPh)_2]$ [7] and $[Co_4(CO)_8(\mu_4\text{-}PPh)_2L_2]$ (L = PPh_3 or CO) [8].

It has been known that the susceptibility of a hydrido cluster to attack by bases depends strongly on the degree of the steric hindrance of the hydride ligands. In trinuclear clusters $[Ru_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}PPh)]$ [3], for example, the μ-H ligand is considered to be very strongly shielded [9]. As a result, only one hydride ligand can be removed as a proton even by very strong bases like KOH, LiBu^n, NaH, KH or Na/Hg. Our studies show that the two hydrides in clusters $[Ru_4(CO)_{13}(\mu\text{-}H)_2(\mu_4\text{-}PCF_3)]$ or $[Ru_4(CO)_{12}(\mu\text{-}H)_2(\mu_3\text{-}PCF_3)_2]$ can be removed by DBU (after deprotonation by excess DBU, there are no hydride signals in their ^1H-NMR spectra). This implies that $[Ru_4(CO)_{13}(\mu\text{-}H)_2(\mu_4\text{-}PCF_3)]$ and $[Ru_4(CO)_{12}(\mu\text{-}H)_2(\mu_3\text{-}PCF_3)_2]$ are relatively strong acids



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Scheme 1. The formation of heterometallic clusters **1** and **2**.

Table 1
Spectroscopic characterization data for **1** and **2**

Cluster	IR (νCO, cm^{-1}) (in hexane)	^{1}H	^{31}P{^{1}H}	^{19}F
1	2069m, 2942s, 2011s, 1968w	1.67(s), 1.64(s)	19.8(s), 356.5(s)	17.7(d)
2	2102w, 2077m, 2057m, 2039s, 2021s, 1986w	7.12–7.73(m)	56.0(m), 66.7(m)	21.5(m)

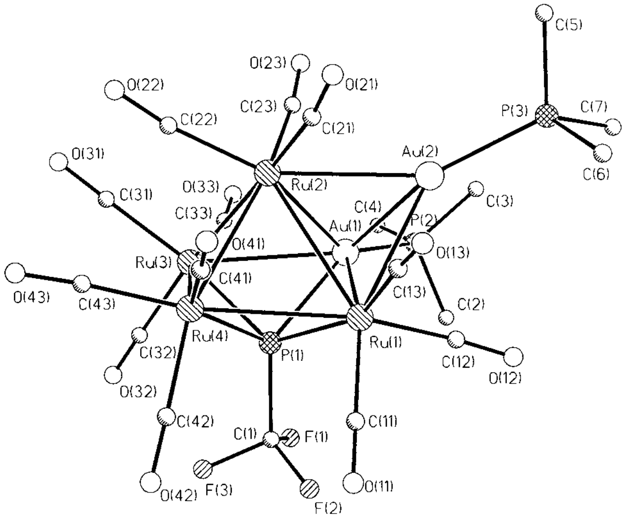

Fig. 1. Molecular structure of **1**.

with the two hydrides easily removal even in the presence of a large base like DBU (Table 1).

2.2. Molecular structure of 1

The structure of **1** is shown in Fig. 1. Selected bond lengths and angles are given in Table 2. The four Ru atoms and Au(1) define an approximate square pyramid configuration with one face [Ru(1)Ru(2)Au(1)] triply capped by Au(2) atom. The Ru atoms adopt a butterfly geometry with four normal Ru–Ru bonds [Ru(1)–Ru(4) = 2.894(2) Å, Ru(2)–Ru(4) = 2.822(2) Å, Ru(3)–Ru(4) = 2.922(2) Å and Ru(2)–Ru(3) = 2.892(2) Å] and one slightly long Ru–Ru bond [Ru(1)–Ru(2) = 3.032(2)Å], which is bridged by Au(2) atom. The elongation of the Ru(1)–Ru(2) bond distance suggests that, at least in this case, the gold phosphine moiety may exert a bond-lengthening influence. The phosphinidene unit lies at the bottom of the distorted square defined by Ru(1), Au(1), Ru(3) and Ru(4). The Au–PMe$_3$ bond distances are similar to the values previously observed in cluster compounds containing AuPR$_3$ fragments, whereas the Au-to-PCF$_3$ interaction seems to be somewhat longer [2.453(3) Å]. The mean value of the Au–Ru bond length is significantly larger than that observed in cluster [Ru$_3$(CO)$_9$(μ-H)(μ$_3$-PPh){Au(PMe$_2$Ph)}] [2.756-(5) Å] [3] but compares well with the value reported for cluster [Ru$_4$(CO)$_{12}$(μ-H)(AuPPh$_3$)$_3$] [2.880(5) Å] [10]. The Au–Au bond distance, 2.826(1) Å, is comparable to that found in [Ru$_4$(CO)$_{12}$(μ-H)(AuPPh$_3$)$_3$] [2.831(4) Å] but noticeably shorter than that published for the cluster [Ru$_3$(CO)$_9$(μ-COMe){Au(PPh$_3$)}$_3$] [2.970(1) Å] [10] and that observed in metallic gold [2.884 Å] [11]. The metal carbonyl angles for **1** range from 169.0(16) to 178.2(18)°, all showing terminal coordination mode. The average Ru–C and C–O bond lengths in the metal carbonyl groups of 1.906(16) and 1.130(21) Å are close to the expected values.

2.3. Molecular structure of 2

The X-ray diffraction structure of **2** is illustrated in Fig. 2. Selected bond lengths and angles are listed in Table 2. The Ru$_4$ metal skeleton has an open chain

Table 2
Selected bond lengths (Å) and angles (°) for **1** and **2**

Cluster **1**			
Au(1)–Au(2)	2.826 (1)	Au(2)–Ru(2)	2.839 (1)
Au(1)–Ru(1)	3.028 (1)	Ru(1)–Ru(4)	2.894 (2)
Au(1)–Ru(2)	2.883 (1)	Ru(2)–Ru(3)	2.892 (1)
Au(1)–Ru(3)	2.900 (1)	Ru(2)–Ru(4)	2.822 (2)
Au(2)–Ru(1)	2.863 (1)	Ru(3)–Ru(4)	2.922 (2)
Ru(1)–Ru(2)	3.032 (2)		
Au(1)–Ru(3)–Ru(4)	90.9(1)	Ru(1)–Au(2)–Ru(2)	64.2(1)
Ru(2)–Ru(3)–Ru(4)	58.1(1)	Au(1)–Ru(2)–Ru(1)	61.5(1)
Ru(3)–Ru(2)–Ru(4)	61.5(1)	Au(2)–Ru(2)–Ru(1)	58.3(1)
Ru(1)–Ru(2)–Ru(4)	59.1(1)	Au(1)–Au(2)–Ru(1)	64.3(1)
Au(2)–Au(1)–Ru(1)	58.4(1)	Au(1)–Au(2)–Ru(2)	61.2(1)
Au(2)–Au(1)–Ru(2)	59.6(1)	Au(1)–Ru(1)–Au(2)	57.3(1)
Ru(1)–Au(1)–Ru(2)	61.6(1)	Au(1)–Ru(1)–Ru(2)	56.8(1)
Au(2)–Au(1)–Ru(3)	119.4(1)	Au(2)–Ru(1)–Ru(2)	57.5(1)
Ru(1)–Au(1)–Ru(3)	88.6(1)	Au(1)–Ru(1)–Ru(4)	89.0(1)
Ru(2)–Au(1)–Ru(3)	60.0(1)	Au(1)–Ru(2)–Au(2)	59.2(1)
Cluster **2**			
Au(1)–Ru(1)	2.776 (1)	Au(2)–P(4)	2.310 (4)
Au(1)–Ru(2)	2.780 (1)	Ru(1)–P(1)	2.391 (4)
Au(2)–Ru(3)	2.776 (1)	Ru(1)–P(2)	2.360 (3)
Au(2)–Ru(4)	2.760 (1)	Ru(2)–P(2)	2.299 (4)
Ru(1)–Ru(2)	3.080 (2)	Ru(3)–P(1)	2.319 (4)
Ru(2)–Ru(3)	2.951 (2)	Ru(4)–P(1)	2.363 (4)
Ru(3)–Ru(4)	3.094 (2)	Ru(4)–P(2)	2.396 (4)
Au(1)–P(3)	2.312 (4)		
Ru(1)–Au(1)–Ru(2)	67.3(1)	Ru(1)–P(1)–Ru(4)	107.8(2)
Ru(3)–Au(2)–Ru(4)	68.0(1)	Ru(3)–P(1)–Ru(4)	82.7(1)
Ru(1)–Ru(2)–Ru(3)	82.5(1)	Ru(1)–P(2)–Ru(2)	82.7(1)
Ru(2)–Ru(3)–Ru(4)	82.1(1)	Ru(1)–P(2)–Ru(4)	107.7(1)
Ru(1)–P(1)–Ru(3)	115.2(1)	Ru(2)–P(2)–Ru(4)	115.5(2)

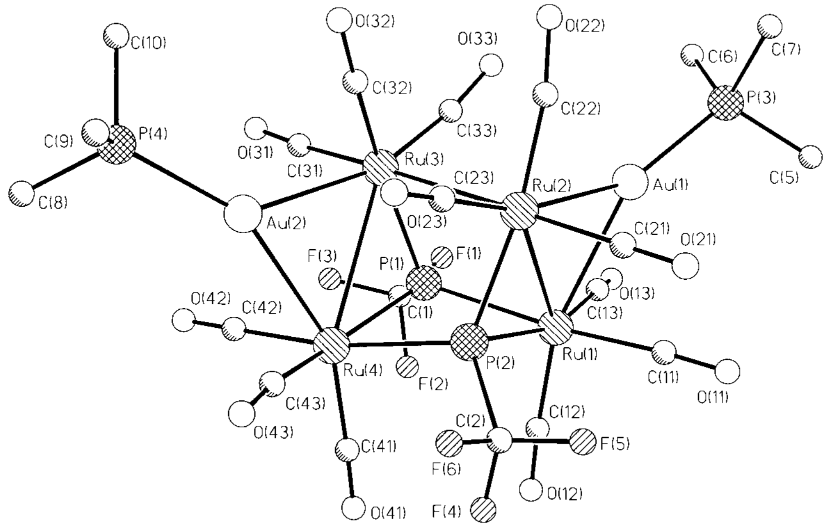

Fig. 2. Molecular structure of 2.

geometry, with two long Ru–Ru bonds each edge-bridged by a $AuPPh_3$ moiety. This structural type has not been found so far for mixed-metal carbonyl clusters. The average Au–P bond length [2.311(1) Å] is similar to the value of 2.279(8) Å in [Ph_3PAuMe][12,13] where the Au^I atom is sp hybridized. This observation is consistent with the assignment of the Au^I atoms in **2** as sp hybridized. The Au–Ru bond lengths [mean 2.773(1) Å] fall in the normal range for Au–Ru bonds.

Table 3
Crystal data and refinement details for **1** and **2**

Cluster	**1**	**2**
Empirical formula	$C_{19}H_{18}O_{12}F_3P_3Ru_4Au_2$	$C_{50}H_{30}O_{12}F_6P_4Ru_4Au_2$
Formula weight	1386.5	1858.8
Crystal size	0.44 × 0.42 × 0.25	0.6 × 0.20 × 0.27
Space group	*C2c*	$P\bar{1}$
a	34.035(7)	10.745(2)
b	9.897(2)	11.360(2)
c	21.442(4)	23.696(5)
α	90	86.92(3)
β	110.96(2)	83.80(3)
γ	90	84.80(3)
U	6744(2)	2860.9(14)
Z	8	2
d (g cm^{-3})	2.731	2.158
μ	10.624	63.26
Temperature	23	23
Scan mode	ω	ω
Scan speed (° min^{-1} in ω)	3.00–16.74	3.00–16.74
Scan range	1.20	1.20
Max. 2θ	48	45
No. of data collected	5078	7785
No. of indept. data	5000	7323
No. of observ. data	4114 [$F_o > 4\sigma(F)$]	5593 [$F_o > 4\sigma(F)$]
No. of parameters	389	524
R	0.0455	0.0481
R_w	0.0550	0.0602
GOF	1.31	1.37
Largest diff. peak (e $Å^{-3}$)	1.93	2.23
Lowest diff. peak (e $Å^{-3}$)	−1.78	−0.85
F(000)	5072	1748

The structure allows a comparison of the bonding ability of a hydride and that of an $AuPR_3$ unit, where the Au atom is considered to be in the −1 formal oxidation state and may be thought of as being sp hybridized with one lobe of an sp orbital pointing at the mid-point of the M–M bond it bridges. In cluster **2**, the P(3)–Au(1)-{midpoint-[Ru(1)–Ru(2)]} angle of 181° is consistent with this hypothesis. This interaction is analogous to that of a bridging hydride and both Au(1) and Au(2) act as one-electron donors. Each ruthenium atom is also ligated by three essentially terminal carbonyl ligands, which show little deviation from linearity.

Another interesting feature of this compound is the relatively weak P–P interaction. The phosphorus–phosphorus separation of 2.661(5) Å is too long to be associated with a phosphorus–phosphorus bond, but this distance is a little shorter than that of cluster [$Ru_4(CO)_{10}(CO)(\mu_4\text{-}PPh)_2$] [2.771 Å] [14] and slightly longer than those found for some iron clusters [15] (Table 3).

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 an FT-IR 2000 spectrophotometer. NMR spectra were obtained on an ACF Bruker 300 MHz spectrometer. The compounds [$Ru_4(CO)_{13}(\mu\text{-}H)_2(\mu_4\text{-}PCF_3)$] and [$Ru_4(CO)_{12}(\mu\text{-}H)_2(\mu_3\text{-}$

$PCF_3)_2]$ were prepared as described previously [16]. The complexes $[Au(PMe_3)Cl]$ and $[Au(PPh_3)Cl]$ were synthesized and isolated as solids from $AuCl_3{\cdot}3H_2O$ solution by adding the appropriate amount of the corresponding phosphine.

3.2. Synthesis of $[Au_2Ru_4(CO)_{12}(\mu_4\text{-}PCF_3)(PMe_3)_2]$ (**1**)

A dichloromethane solution (10 ml) of $[Ru_4(CO)_{13}(\mu\text{-}H)_2(\mu_4\text{-}PCF_3)]$ (0.08 g, 0.092 mmol) and $[Au(PMe_3)Cl]$ (0.068 g, 0.18 mmol) was placed in a reaction tube and degassed. DBU (0.03 ml, 0.20 mmol) was added by injection whereupon a brown solution immediately formed. The mixture was allowed to reaction at room temperature (r.t.) for 2 h. After removing the solvent in vacuo, the reddish–brown solid was extracted with CH_2Cl_2 and subjected to TLC using dichloromethane–hexane as eluent (1:2, v/v). The major red band (R_f = 0.37) of **1** was extracted with dichloromethane as the major product (ca. 22%). Elemental analysis of **1** gave C 16.66, H 1.67, P 6.93, F 4.29. Anal. Calc. C 16.45, H 1.30, P 6.71, F 4.11%.

3.3. Synthesis of $[Au_2Ru_4(CO)_{12}(\mu_3\text{-}PCF_3)_2(PPh_3)_2]$ (**2**)

The cluster $[Ru_4(CO)_{12}(\mu\text{-}H)_2(\mu_3\text{-}PCF_3)_2]$ (0.094 g, 0.10 mmol) and $[Au(PPh_3)Cl]$ (0.10 g, 0.20 mmol) were degassed with 10 ml of dichloromethane in a reaction vessel using three cycles of the freeze–pump–thaw technique. The mixture was then treated with DBU (0.03 ml, 0.20 mmol) upon which a colour change from yellow to brown occurred. After stirring at r.t. for 24 h, the solvent was removed in vacuo and the solid extracted with dichloromethane and subjected to TLC using dichloromethane–hexane (1:2, v/v) as eluent. Cluster **2** (R_f = 0.76) was isolated as major product (ca. 21%). Elemental analysis of **2** gave C 32.62, H 1.81, P 7.15, F 5.55. Anal. Calc. C 32.29, H 1.61, P 6.67, F 6.13%.

3.4. X-ray structure determination

Crystal data and details of measurement for compounds **1** and **2** are given in Table 2. Diffraction intensities were collected at 298 K on a Siemens R3m/V X-ray diffractometer with graphite-monochromatised Mo–K_α radiation ($\lambda = 0.71073$ Å). All computions were carried out using the SHELXTL PLUS (PC version) program package [17]. 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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