Synthesis and characterization of triosmium and triruthenium pyrene clusters

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ABSTRACT

The reaction between 1-pyrenecarboxaldehyde ($C_{16}H_9CHO$) and the labile triosmium cluster $[Os_3(CO)_{10}(CH_3CN)_2]$ gives rise to the formation of two new compounds by competitive oxidative addition between the aldehydic group and an arene C–H bond, to afford the acyl complex $[Os_3(CO)_{10}(\mu-H)(\mu-COC_{16}H_9)]$ (1) and the compound $[Os_3(CO)_{10}(\mu-H)(C_{16}H_8CHO)]$ (2), respectively. Thermolysis of $[Os_3(CO)_{10}(\mu-H)(\mu-C_{16}H_9CO)]$ (1) in n-octane affords two new complexes in good yields, $[Os_3(CO)_9(\mu-H)_2(\mu-COC_{16}H_8)]$ (3) and the pyryne complex $[Os_3(CO)_9(\mu-H)_2(\mu_3-\eta^1:\eta^1:\eta^2-C_{16}H_8)]$ (4).

In contrast, when 1-pyrenecarboxaldehyde reacts with $[Ru_3(CO)_{12}]$ only one product is obtained, $[Ru_3(CO)_9(\mu-H)_2(\mu_3-\eta^1:\eta^1:\eta^2-C_{16}H_8)]$ (5), a nonacarbonyl cluster bearing a pyrene ligand. All compounds were characterized by analytical and spectroscopic data, and crystal structures for 1, 2, 4 and 5 were obtained.

1. Introduction

Polycyclic aromatic hydrocarbons (PAH) constitute an important group of enviromental pollutants and are invariably generated during incomplete combustion [1]. Polycyclic aromatic systems contain a large number of π electrons formally available for interacting with transition metals and have been shown to coordinate in a wide variety of bonding modes [2]. Research on the incorporation of arenes into clusters has largely been stimulated by their potential as models for chemisorption on metal surfaces and by the wish to modify arene structures and reactivity [3,4]. The chemistry of benzene with metal clusters has been developed extensively in recent years, [5] where dominant modes of coordination are η⁶- at a single metal atom, $\mu_3-\eta^2:\eta^2:\eta^2$- over a triangular cluster face, or combinations of these two modes with σ-M–C bonding. Several of these modes resemble chemisorption of benzene on a (1 1 1) surface or on step-sites on such surfaces [6–8].

Studies of the compounds mentioned above are often hindered by the difficulty of introducing PAH into the coordination sphere of the cluster, i.e., naphtalene and anthracene have been introduced into a triruthenium cluster by thermal degradation of a tertiary phosphine. However the cluster compounds obtained retained the original P–C (arene) bond or where the P–C (arene) bond is cleaved, the heteroatom remains coordinated at the metal centres [9,10].

In this work, we describe the synthesis of several new triosmium clusters derived from the reaction of the reactive species $[Os_3(CO)_{10}(CH_3CN)_2]$ with 1-pyrenecarboxaldehyde. Also the reac-

tion of $[Ru_3(CO)_{12}]$ with 1-pyrenecarboxaldehyde was undertaken. The aldehyde reacts at the unsaturated C–C bond of the arene, at the –CHO group, or at both.

2. Experimental

All reactions and manipulations were routinely carried out by using standard schlenk, vacuum line and syringe techniques under an atmosphere of oxygen-free Ar or N_2. All solvents for synthetic use were reagent grade. Hexane was dried and distilled over sodium in the presence of benzophenone under an Ar atmosphere; CH_2Cl_2 was dried and distilled over CaH_2, Na and $MgSO_4$. Column chromatography was performed by using silica gel 60 (Merck) and preparative TLC on 20×20 cm glass plates coated with silica gel 60 HF254 (2 mm thick). Triosmium and triruthenium carbonyls (Strem) and 1-pyrenecarboxaldehyde (Aldrich) were used as received. Trimethylamine-N-oxide (Aldrich) was sublimed prior to use and stored under Ar. The labile derivative $[Os_3(CO)_{10}(CH_3CN)_2]$ was prepared according to literature procedures [11].

^{1}H, ^{13}C, COSY and HMQC experiments were undertaken on Bruker Avance-300 and -500 instruments. IR spectra were recorded on a Nicolet 5DXC and elemental analysis was obtained on a Carlo Erba Fisson 1108. X-ray diffraction studies were performed on a Rigaku AFC-7S diffractometer with a Bruker Smart Apex area detector.

2.1. Reaction of $[Os_3(CO)_{10}(CH_3CN)_2]$ with 1-pyrenecarboxaldehyde

A solution of $[Os_3(CO)_{10}(CH_3CN)_2]$ (100 mg, 0.107 mmol) and 1-pyrenecarboxaldehyde (24 mg, 0.104 mmol) in cyclohexane (50 ml) was heated under reflux under N_2 for 4 h. Removal of the

solvent under vacuum and separation of the residue by TLC (eluant: hexane/CH_2Cl_2:4/1) gave two bands. The main band gave $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-COC}_{16}H_9)]$ (**1**) (55 mg, 45%) as a yellow solid; the second band, $[Os_3(CO)_{10}(\mu\text{-H})(C_{16}H_8CHO)]$ (**2**) (28 mg, 25%), gave a red solid. In both cases, crystals suitable for X-ray diffraction studies were obtained from cyclohexane. Anal. Calc. for $C_{27}H_{10}O_{11}Os_3$: C, 29.89; H, 0.92. Found for **1**: C, 29.4; H, 0.90%. Found for **2**: C, 29.5; H, 0.89%.

2.2. Thermolysis of compound **1**

A solution of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-COC}_{16}H_9)]$ (**1**) (50 mg, 0.043 mmol) in *n*-octane (50 mL) was heated under reflux under N_2 for 5 h. Removal of the solvent under vacuum and TLC separation as above gave two yellow bands, characterized as $[Os_3(CO)_9(\mu\text{-H})_2(\mu\text{-COC}_{16}H_8)]$ (**3**) (12 mg, 30%) and $[Os_3(CO)_9(\mu\text{-H})_2(\mu_3\text{-}\eta^1:\eta^1:\eta^2\text{-C}_{16}H_8)]$ (**4**) (10 mg, 22%). Crystals of **4** suitable for X-ray analysis were obtained by slow evaporation from *n*-hexane. Anal. Calc. for $C_{26}H_{10}O_{10}Os_3$: C, 29.66; H, 0.95. Found for **3**: C, 29.2; H, 0.92%. Anal. Calc. for $C_{25}H_{10}O_9Os_3$: C, 29.29; H, 0.98. Found for **4**: C, 28.9; H, 0.95%.

### 2.3. Reaction of [Ru₃(CO)₁₂] with 1-pyrenecarboxaldehyde

A solution of $[Ru_3(CO)_{12}]$ (100 mg, 0.156 mmol) and 1-pyrene-carboxaldehyde (72 mg, 0.313 mmol) in cyclohexane (60 ml) was heated under reflux under N_2 for 24 h. Removal of the solvent under vacuum and separation of the residue by TLC (eluant: hexane/CH_2Cl_2:4/1) gave $[Ru_3(CO)_9(\mu\text{-H})_2(\mu_3\text{-}\eta^1:\eta^1:\eta^2\text{-C}_{16}H_8)]$ (**5**) (45 mg, 40%), as yellow crystals from *n*-hexane. Anal. Calc. for $C_{25}H_{10}O_9Ru_3$: C, 39.64; H, 1.32. Found for **5**: C, 39.12; H, 1.29%.

3. Results and discussion

The reaction of the labile cluster $[Os_3(CO)_{10}(CH_3CN)_2]$ with 1-pyrenecarboxaldehyde under moderate conditions affords the compounds $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-COC}_{16}H_9)]$ (**1**) and $[Os_3(CO)_{10}(\mu\text{-H})(C_{16}H_8CHO)]$ (**2**) in good yields (Scheme 1), characterized by IR and NMR spectroscopy (Table 1). The ^{1}H NMR spectra of both **1** and **2** exhibit resonances in the aromatic and hydride regions. The IR spectrum of compound **1** is analogous to known μ-acyl derivatives [12] and its ^{1}H NMR spectrum in the aromatic region shows resonances due to the unaltered pyrene ring; the resonance of the aldehydic proton is absent and the bridging hydride is observed at δ −13.2 ppm.

The formyl group is preserved in compound **2** as shown by the ^{1}H NMR spectrum (δ CHO = 10.9 ppm), so the compound is structurally comparable to $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-MeC=CHCOMe})]$ [13] and the aldehydic derivatives $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-RC=CHCHO})]$ [12] which contain chelating a,b-unsaturated ketones and aldehydes, respectively. The behaviour of 1-formylpyrene with $[Os_3(CO)_{10}(CH_3CN)_2]$ is very like that of 2-formyl-thiophene, with
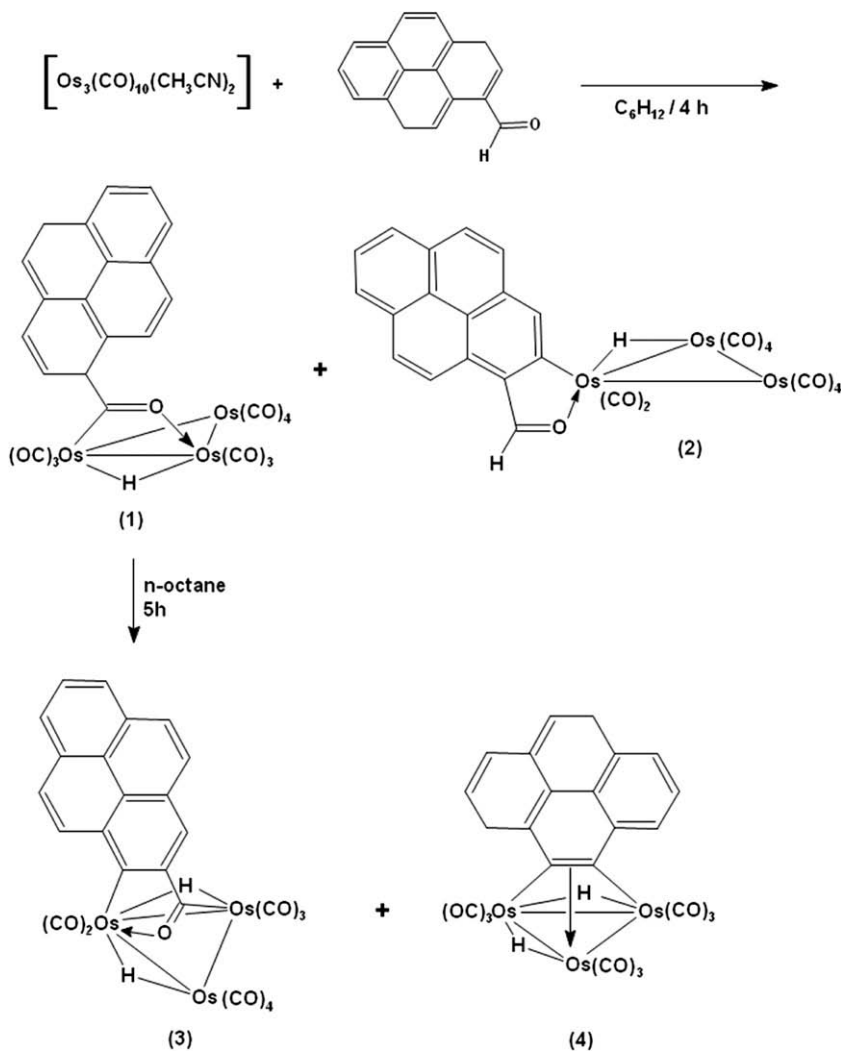
Scheme 1.

Table 1
Spectroscopic data for clusters **1**–**5**.

| Compound	ν (CO)[a] (cm^{-1})	^{1}H NMR (δ, ppm)	J (Hz)
$[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}COC_{16}H_9)]$ (**1**)	2107 w	8.63 (d, H_a)[b]	ab 9.4
	2067 s	8.60 (d, H_i)	cd 8.9
	2057 s	7.99; 7.94 (dd, H_e, H_g)	ef = eg = fg 7.6
	2025 s	7.98 (d, H_b)	hi 8.2
	2017 s	7.88; 7.68 (d, H_c, H_d)	
	1995 m	7.84 (d, H_h)	
	1980 w	7.77 (ddd, H_f)	
	1432 w	−13.2 (s, OsH)	
$[Os_3(CO)_{10}(\mu\text{-}H)(C_{16}H_8CHO)]$ (**2**)	2127 w	10.99 (s, CHO)[c]	cd 9.1
	2068 m	9.00 (d, H_c)	ef = eg = fg 7.6
	2049 s	8.75 (s, H_b)	hi 9.0
	2021 s	8.38; 8.32 (d, H_e, H_g)	
	2007 m	8.37 (d, H_d)	
	1992 m	8.30; 8.09 (d, H_h, H_i)	
	1983 w	8.03 (ddd, H_f)	
	1935 w	−11.6 (s, OsH)	
	1430 w		
$[Os_3(CO)_9(\mu\text{-}H)_2(\mu\text{-}COC_{16}H_8)]$ (**3**)	2127 w	9.16 (s, H_b)[b]	cd 8.9
	2080 m	8.16 (d, H_e)	ef = eg = fg 7.6
	2070 m	8.13 (d, H_d)	hi 8.9
	2050 s	7.98 (d, H_g)	
	2032 m	7.93 (d, H_i)	
	2020 m	7.82 (dd, H_f)	
	2006 m	7.70 (d, H_h)	
	1993 m	7.62 (d, H_c)	
	1976 m	−13.0 (s, OsH), −15.5 (s, OsH)	
$[Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C_{16}H_8)]$ (**4**)	2105 m	8.13 (dd, 2H_a)[d]	ab 7.7
	2080 f	8.09 (dd, 2H_c)	ac 1.0
	2055 f	8.03 (s, 2H_d)	bc 7.7
	2034 f	7.97 (dd, 2H_b)	
	2028 m	−16.0 (s, RuH)[e]	
	2009 m	−19.0 (s, RuH)[e]	
	2003 m		
	1984 m		
$[Ru_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C_{16}H_8)]$ (**5**)	2104 m	8.40 (dd, 2H_a)[c]	ab 7.7
	2078 s	8.23 (dd, 2H_c)	ac 1.0
	2056 s	8.12 (s, 2H_d)	bc 7.7
	2044 s	8.04 (dd, 2H_b)	
	2027 m	−14.7 (s, RuH)[e]	
	2011 s	−18.2 (s, RuH)[e]	
	1991 m		

[a] C_6H_{12}.
[b] C_6D_6.
[c] $(CD_3)_2CO$.
[d] CD_2Cl_2.
[e] At 188 K.

competitive C–H cleavage at the –CHO group and at the ring site [14]. Compounds **1** and **2** can be identified by comparison of their ν(CO) absorption patterns to those of related acyl and chelate complexes [12]. The ^{1}H NMR and IR data for compounds **1** and **2** (Table 1) unambiguously support the structures given. **1** and **2** exhibit seven absorptions in the terminal carbonyl stretching region (2127–1970 cm^{-1}), and the spectra are similar to those observed for previously reported analogous compounds derived from 2-formyl-thiophene and -furan for the coordinated organic carbonyl; the IR absorption for **1** at 1432 cm^{-1} and at 1430 cm^{-1} for **2** confirm that acyl groups are coordinated.

The structures depicted in Scheme 1 for compounds **1** and **2** were confirmed by X-ray diffraction studies (Figs. 1 and 2). In compound **1** the acyl ligand lies over one edge of the metal triangle, which is slightly longer than the others due to the acyl coordination Os(1)–Os(3) = 2.8894(15) Å. The pyrene group is linked to the $Os_3H(CO)_{10}$ moiety through the carbonyl C(1)–O(1) (Table 2); the pyrene-CO ligand relates directly to other μ-acyl ligands such as phenacyl ($PhCH_2CO$) [15]. The strongest contact between the acyl and the metal atoms is through C(1), where the bond trans to it [Os(1)–C(13A) = 2.01(3) Å] is much larger than the bond trans to O(1) [Os(3) –C (32A) = 1.87(2) Å] (see Fig. 1).

For compound **2** crystals suitable for X-ray diffraction studies were obtained by slow evaporation from cyclohexane at room temperature. Compound **2** is structurally related to $[Os_3(CO)_{12}]$ with the pyrenealdehyde chelate replacing two CO ligands (the aldehyde group axially coordinated) and a bridging hydride ligand (Fig. 2). Although the hydride was not detected, the long Os(2)–Os(3) distance [3.0219(10) Å] (Table 3) and the large Os–Os–CO equatorial angles associated with this Os–Os contact [Os(3)–Os(2)–C(23) = 117.0(5) and Os(2)–Os(3)–C(32) = 112.2(5)°] indicate that the hydride bridges these osmium atoms. The hydride therefore, lies trans to the Os–C σ-bond of the chelate and presumably close to the Os3 plane. The CO ligands are axially and equatorially oriented as in $[Os_3(CO)_{12}]$, while the axial CO trans to the aldehydic oxygen atom experiences greater π donation from osmium and is associated with a shorter Os–C bond [Os(3)–C(31) = 1.87(2) Å] than the other CO ligands [Os(1)–C(11) = 1.99(2); Os(1)–C(13) = 1.96(2); Os(2)–C(21) = 2.05(2) and Os(2)–C(22) = 1.95(2) Å].
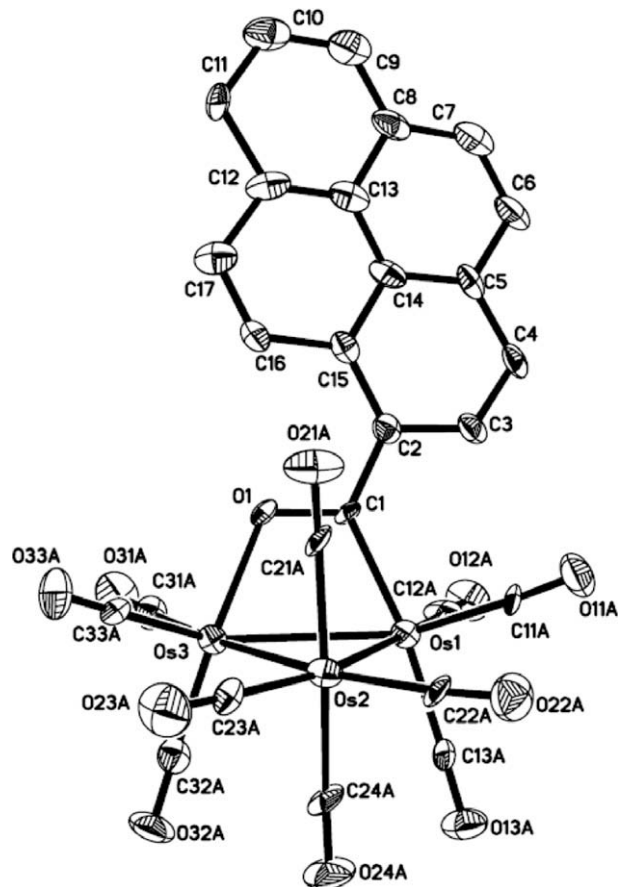
Fig. 1. ORTEP diagram for the molecular structure of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}COC_{16}H_9)]$ (**1**). H atoms omitted for clarity.
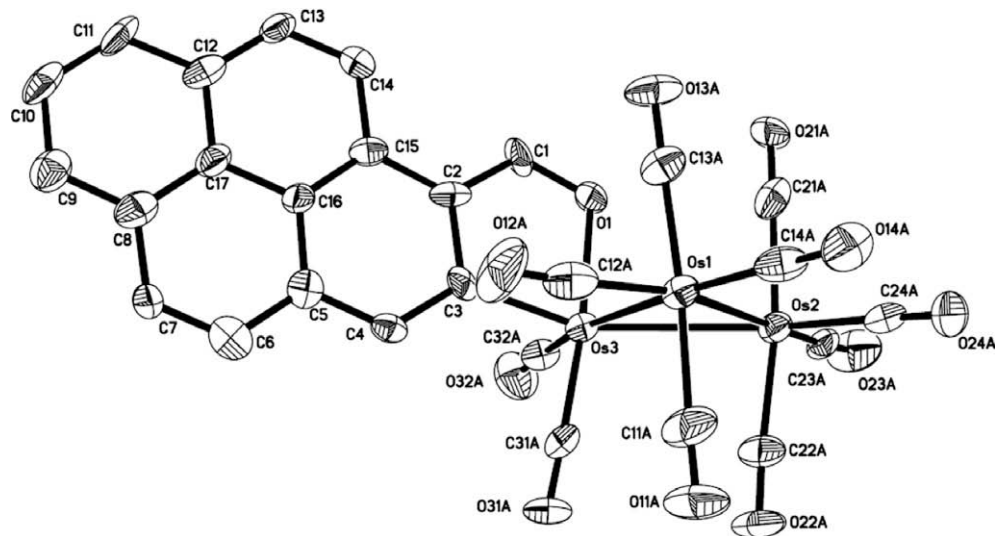
Fig. 2. ORTEP diagram for the molecular structure of [Os$_3$(CO)$_{10}$(μ-H)(C$_{16}$H$_8$CHO)] (**2**). H atoms omitted for clarity.

Thermolysis of [Os$_3$(CO)$_{10}$(μ-H)(μ-COC$_{16}$H$_9$)] (**1**) in *n*-octane for 5 h affords the compounds [Os$_3$(CO)$_9$(μ-H)$_2$(μ-COC$_{16}$H$_8$)] (**3**) (30% yield) and [Os$_3$(CO)$_9$(μ-H)$_2$(μ$_3$-η^1:η^1:η^2-C$_{16}$H$_8$)] (**4**) (20% yield) as shown in Scheme 1.

All efforts to obtain good quality crystals for compound **3** were unsuccessful, but the spectroscopic evidence supports the proposed structure for **3** in Scheme 1. Its ^{1}H NMR spectrum shows eight resonances in the range of δ 7.62–9.16 corresponding to eight pyrene ring protons (Table 1) and two hydride resonances at δ −13.04 and −15.5 coupled to each other. HMQC studies unambiguously show the long range coupling between the acyl carbon (^{13}C δ 154 ppm) and the β-(H^b) singlet (δ 9.16 ppm). As for compound **2**, the IR spectrum of **3** shows a band in 2127 cm^{-1}, a characteristic

high frequency value only found for chelate–CO bonding modes in related Os clusters [12]. Decarbonylation at the metal and ortho-metallation of the pyrene ring give rise to a nonacarbonyl compound where the (μ-COC$_{16}$H$_8$) ligand acts as a 4-electron donor (see Scheme 1, Table 1).

The other nonacarbonyl compound [Os$_3$(CO)$_9$(μ-H)$_2$(μ$_3$-η^1:η^1:η^2-C$_{16}$H$_8$)] (**4**) was obtained in 22% yield. Its X-ray structure shows that there are three Os-Os bonds and the pyrene ligand is bound through two σ-bonds and a η^2-coordination to the third osmium atom (Fig. 3). The ^{1}H NMR spectrum at room temperature shows only four resonances in the aromatic region, accounting for eight protons, indicating a symmetrical bonding of the pyrene unit. At high field, a two-hydride singlet is observed; on lowering the
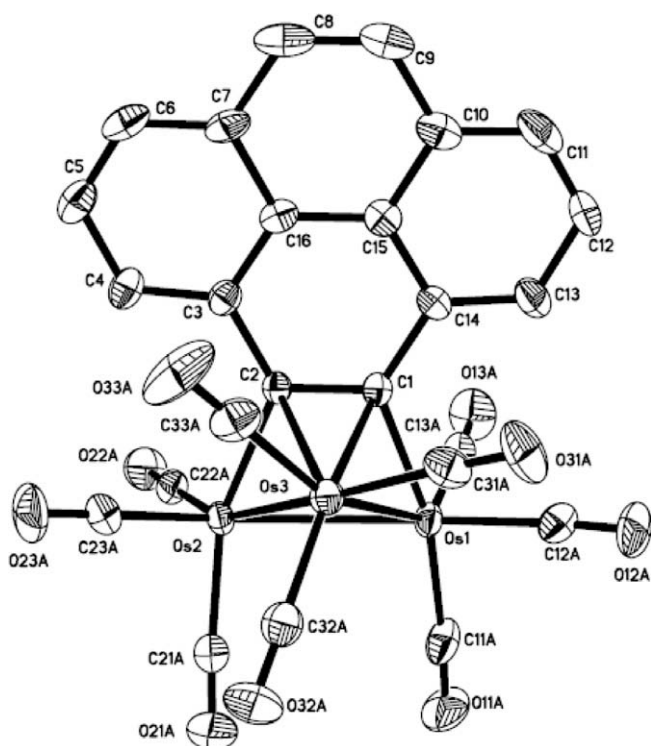
Fig. 3. ORTEP diagram for the molecular structure of [Os$_3$(CO)$_9$(μ-H)$_2$(μ$_3$-η^1:η^1:η^2-C$_{16}$H$_8$)] (**4**). H atoms omitted for clarity.
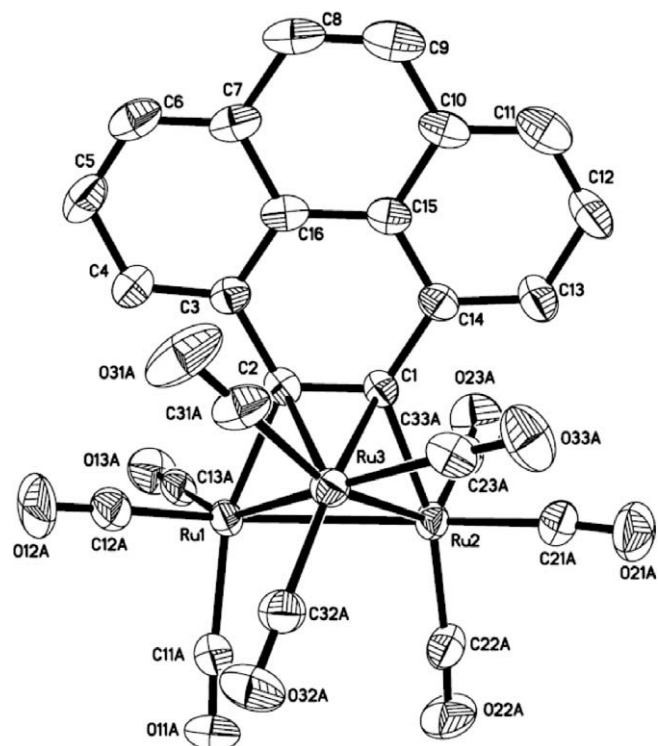
Fig. 4. ORTEP diagram for the molecular structure of [Ru$_3$(CO)$_9$(μ-H)$_2$(μ$_3$-η^1:η^1:η^2-C$_{16}$H$_8$)] (**5**). H atoms omitted for clarity.
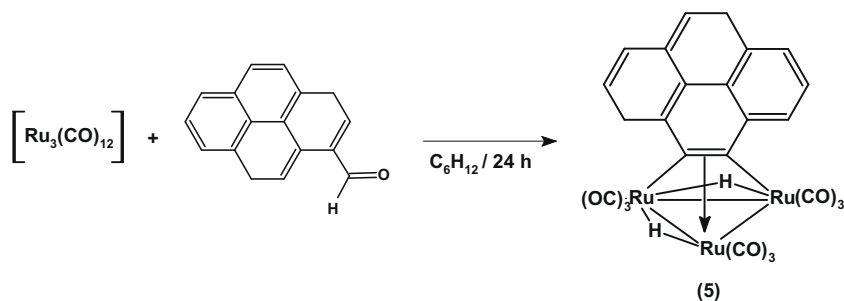
Scheme 2.

temperature to 188 K two signals are obtained at δ −16.0 and −19.0 ppm, showing that hydride exchange in the triangle presumably occurs more slowly than the $C_{16}H_8$ rotation, the former occurring by rapid hydride transfer to the vacant edge of the Os_3 triangle. We do not know the mechanism of hydrogen transfer to obtain compound **4** from compound **1**, but as in so many transition-metal organometallic reactions a reversible transfer of hydrogen atoms between and carbon atoms would seem the most obvious.

In **4**, the pyryne ligand lies over one face of the metal triangle such that the dihedral angle between the plane of the ring and that of the metal triangle is 60.6°. The organic ring forms σ bonds through C(1) and C(2) to two of the osmium atoms, bridging the Os(1)–Os(2) edge and the C(1)–C(2) bond interacts in a π fashion with the third osmium atom, Os(3). The nine carbonyl ligands are essentially linear [mean M–C–O = 176.98(9)°] and are terminally coordinated to each metal atom, six in pseudo-equatorial positions with respect to the metal triangle and three in axial orientations. The two hydrides were not located directly, but for the analysis of the X-ray diffraction studies they bridge Os(1)–Os(2) and Os(1)–Os(3) bonds (Table 4), being well established that a bridging hydride is concomitant with a longer metal–metal distance in the absence of other bridging groups [16]. For the triosmium pyryne cluster **4**, to be considered a 48 electron system the pyryne must

act as a four-electron donor, which is achieved by donating two electrons through a π bond to Os(3) and one electron each from C(1) and C(2) to Os(1) and Os(2), respectively, *via* two σ-bonds. Despite the apparent donation from the C(1)–C(2) bond there are not significant variations in the C–C bond distances of the six-membered ring bonded to the cluster [mean C–C = 1.440(10) Å] compared to C–C bond distances in the benzyne cluster $[Os_3(CO)_9(\mu-H)_2(\mu_3-\eta^1:\eta^1:\eta^2-C_6H_4)]$ [mean = 1.43(7) Å] [17].

The reaction of $Ru_3(CO)_{12}$ and pyrenecarboxaldehyde (Scheme 2) affords only one compound characterized as $[Ru_3(CO)_9(\mu-H)_2(\mu_3-\eta^1:\eta^1:\eta^2-C_{16}H_8)]$ (**5**), by IR, ^1H NMR and X-ray diffraction studies (Fig. 4). The ^1H NMR of compound **5**, as in the case of compound **4**, shows in the aromatic region only four resonances which indicate a symmetrical bonding of the pyryne ligand; at high field and at 188 K the two hydride signals are separated at δ −14.7 and −18.2 ppm (Table 1). The organic ring forms two σ bonds through C(1) and C(2) to two Ru atoms, bridging the Ru(1)–Ru(2) edge (Table 5), and the C(1)–C(2) bond interacts with the third ruthenium atom in a π fashion, so the pyryne moiety acts as a four-electron donor to give a 48 electron system. As in the case of compound **4**, the carbonyl ligands are essentially linear [mean M–C–O = 177.3(8)°], and there are not significant variations in the C–C bond distances of the six-membered ring bonded to the metallic triangle [mean = 1.441(11) Å].

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

Os(1)–Os(2)	2.8939(11)	Os(2)–Os(1)–C(1)	89.1(6)
Os(1)–Os(3)	2.8994(15)	Os(3)–Os(1)–C(1)	67.2(7)
Os(2)–Os(3)	2.8528(13)	Os(1)–Os(3)–O(1)	67.7(4)
Os(1)–C(1)	2.13(2)	Os(2)–Os(3)–O(1)	89.6(4)
Os(3)–O(1)	2.15(2)	Os(1)–C(1)–O(1)	114(1)
C(1)–O(1)	1.26(2)	Os(1)–C(1)–C(2)	129(2)
C(1)–C(2)	1.46(3)	C(1)–C(2)–C(3)	117(2)
C(2)–C(15)	1.43(3)	C(1)–C(2)–C(15)	126(2)
C(2)–C(3)	1.41(3)	Os(3)–O(1)–C(1)	111(1)
C(3)–C(4)	1.38(3)		
C(4)–C(5)	1.46(4)		
C(5)–C(14)	1.43(3)		
C(14)–C(15)	1.43(3)		

Table 3
Selected bond lengths (Å) and angles (°) for compound **2**.

Os(1)–Os(2)	2.9165(8)	Os(1)–Os(3)–O(1)	90.5(3)
Os(1)–Os(3)	2.8810(10)	Os(1)–Os(3)–C(3)	98.6(4)
Os(2)–Os(3)	3.0219(10)	Os(2)–Os(3)–C(3)	153.6(4)
Os(3)–C(3)	2.059(15)	Os(2)–Os(3)–O(1)	86.3(3)
Os(3)–O(1)	2.144(10)	C(3)–Os(3)–O(1)	79.5(5)
O(1)–C(1)	1.338(19)	Os(3)–O(1)–C(1)	110.7(9)
C(1)–C(2)	1.37(2)	Os(3)–C(3)–C(2)	113(1)
C(2)–C(3)	1.41(2)	Os(3)–C(3)–C(4)	131(1)
C(2)–C(15)	1.44(2)		
C(3)–C(4)	1.41(2)		

Table 4
Selected bond lengths (Å) and angles (°) for compound **4**.

Os(1)–Os(2)	2.9751(6)	Os(2)–Os(1)–C(1)	67.9(2)
Os(1)–Os(3)	2.8599(7)	Os(1)–Os(2)–C(2)	68.9(2)
Os(2)–Os(3)	2.7484(7)	C(1)–Os(3)–C(2)	35.4(2)
Os(1)–C(1)	2.155(7)	Os(1)–C(1)–C(2)	110.8(5)
Os(2)–C(2)	2.111(7)	Os(1)–C(1)–Os(3)	80.0(3)
C(1)–C(2)	1.410(10)	Os(2)–C(2)–Os(3)	76.1(2)
C(1)–C(14)	1.482(10)	Os(2)–C(2)–C(1)	112.0(5)
C(2)–C(3)	1.483(10)	Os(3)–C(1)–C(2)	74.0(4)
C(3)–C(16)	1.411(11)	Os(3)–C(2)–C(1)	70.5(4)
C(14)–C(15)	1.430(11)		
C(15)–C(16)	1.424(11)		

Table 5
Selected bond lengths (Å) and angles (°) for compound **5**.

Ru(1)–Ru(2)	2.9380(11)	Ru(2)–Ru(1)–C(1)	68.0(2)
Ru(1)–Ru(3)	2.8386(13)	Ru(1)–Ru(2)–C(2)	68.8(2)
Ru(2)–Ru(3)	2.7158(12)	C(1)–Ru(3)–C(2)	35.1(2)
Ru(1)–C(2)	2.145(7)	Ru(1)–C(1)–C(2)	110.4(5)
Ru(2)–C(1)	2.097(7)	Ru(1)–C(1)–Ru(3)	79.9(2)
C(1)–C(2)	1.381(10)	Ru(2)–C(2)–Ru(3)	75.9(2)
C(1)–C(14)	1.471(10)	Os(2)–C(2)–C(1)	112.3(5)
C(2)–C(3)	1.498(10)	Ru(3)–C(1)–C(2)	74.0(4)
C(3)–C(16)	1.426(11)	Ru(3)–C(2)–C(1)	71.0(4)
C(14)–C(15)	1.431(11)		
C(15)–C(16)	1.440(12)		

The new clusters so obtained demonstrate that the presence of a formyl substituent in pyrene could be used as an easy way to incorporate the PAH into the coordination sphere of a trimetallic cluster; research on the structure and reactivity of related arene derivatives are being carried out in our lab.

Acknowledgement

Appendix A. Supplementary material

CCDC 708307, 708308, 708309 and 708310 contains the supplementary crystallographic data for compounds **1**, **2**, **3** and **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.01.013.

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