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Reactions of the alkylidyne cluster $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4\text{-}CH{=}CH_2)]$. Crystal structures of $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4\text{-}CH{=}CH_2)]$, $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4\text{-}\mu\text{-}\eta^2\text{-}CH{=}CH)Os_3(\mu\text{-}H)(CO)_{10}]$ and $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4\text{-}C(O)CH_3)]$

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Abstract

The neutral triosmium alkylidyne cluster $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4\text{-}CH{=}CH_2)]$ (**1**) has been made in good yield by the reaction of $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCl)]$ with one equivalent of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the presence of an excess of 4-vinylpyridine. The reaction of **1** with $[Os_3(CO)_{10}(NCMe)_2]$ in refluxing *n*-hexane affords the linked cluster $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4\text{-}\mu\text{-}\eta^2\text{-}CH{=}CH)Os_3(\mu\text{-}H)(CO)_{10}]$ (**2**) in moderate yield, while the Wacker-type reaction of **1** with a trace amount of water in the presence of Wilkinson's catalyst $RhCl(PPh_3)_3$ in refluxing dichloromethane yields the 4-acetylpyridine derivative of the corresponding alkylidyne cluster $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4\text{-}C(O)CH_3)]$ (**3**). The structures of compounds **1**–**3** have been determined by single crystal X-ray diffraction studies. The structure of **1** involves a triosmium alkylidyne metal core with the 4-vinylpyridine moiety bonded to the μ_3-bridging alkylidyne carbon atom. In the case of **2** the triosmium alkylidyne metal core is linked to another triosmium cluster unit via a 4-vinylpyridine moiety, while **3** contains an alkylidyne metal core with the 4-acetylpyridine ligand attached to the apical carbon atom. The M.L.C.T. transitions of all three complexes show strong solvent dependency, displaying unusually large negative solvatochromism in a wide range of organic solvents. This suggests that a less polar excited state is produced by photoexcitation.

Keywords: Osmium; Carbonyl; Cluster; Alkylidyne; Solvatochromism; Crystal structure

1. Introduction

Various pyridines [1] and alkenes [2] have been shown to be good monodentate ligands in triosmium cluster chemistry. Possessing two functional centres, 4-vinylpyridine has the potential of acting as a linking group between cluster units and facilitating cluster build-up. The isolation of the 4-vinylpyridine-substituted triosmium alkylidyne carbonyl cluster has recently been reported [3]. This metal cluster complex can serve as a ligand and bond to another cluster fragment to form a new homonuclear or heteronuclear linked species. Such compounds are thought to be good intermediates in the synthesis of high-nuclearity cluster complexes.

Current interest in the hydroformylation of olefins via rhodium catalysts [4] prompted us also to investigate the possible reaction of **1** with water and oxygen in the presence of Wilkinson's catalyst at atmospheric pressure under mild conditions. Preliminary results reveal a Wacker-type oxidation of the vinyl group in **1** to yield the corresponding acetyl group.

2. Results and discussion

The reaction of $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCl)]$ with one equivalent of DBU in dichloromethane in the presence of a ten-fold excess of 4-vinylpyridine at room tempera-

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Table 1
$^{13}C\{^1H\}$ NMR data for the cluster 1 and the ligand 4-vinylpyridine, δ (ppm) [a]

Cluster 1	4-vinylpyridine
166.0 (s, C_3 or $2C_5$)	150.2 (s, $2C_5$)
148.4 (br, 9CO)	144.8 (s, C_3)
147.4 (s, C_3 or $2C_5$)	134.8 (s, C_2)
133.2 (s, C_2)	120.8 (s, $2C_4$)
124.6 (s, $2C_4$)	118.6 (s, C_1)
123.8 (s, C_1)	
30.1 (s, C_6)	

[a] CD_2Cl_2.

ture gives the red crystalline compound $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4\text{-}CH{=}CH_2)]$ (1) (ca. 69% yield). Complex 1 has been fully characterised by spectroscopic methods [3]. The $^{13}C\{^1H\}$ NMR data at room temperature for 1 and the free ligand [5] are given in Table 1, and Fig. 1 shows the numbering schemes used. A broad resonance (at ca. δ148.4), attributable to the nine carbonyl ligands, was observed at room temperature, and is attributable to the rapid intramolecular scrambling of the carbonyl ligands [6,7]. Furthermore, the methylidyne carbon shows an upfield resonance at δ 30.1 in CD_2Cl_2. This shift is similar to that reported for the compound $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_5)]$ [8], and may be taken as an indication of the electron richness of the "Os_3C" core in 1.

Single crystals of 1 suitable for diffraction studies were grown by evaporation of a n-hexane/CH_2Cl_2 solution of 1 during 2 days at room temperature. The molecular structure of 1 together with its atom labelling scheme is shown in Fig. 2, and selected bond distances and bond angles are listed in Table 2. The structure of 1 involves a triosmium alkylidyne metal core with the 4-vinylpyridine bonded to the apical carbon atom. The Os–C (alkylidyne) bond lengths are essentially equivalent. The resonance at $\delta - 18.96$ in the ^1H NMR spectrum of 1 shows the presence of metal hydrides [3]. Potential energy calculations suggested that one hydride atom bridges the Os(1)–Os(2) edge and the other the Os(2)–Os(3) edge [9]. These two edges (average 2.868 Å) are significantly longer than the Os(1)–Os(3) bond [2.758(1) Å]. The vinyl fragment C(7)–C(8) is two-fold disordered about the C(4)–C(7) axis with C(7)–C(8) = 1.40(10) Å and C(7)–C(8A) = 1.38(8) Å. [C(8A) is the alternative position of C(8)]. The bond C(4)–C(7) is a single bond [1.52(5) Å], and the angle C(4)–C(7)–C(8) is 121(5)° [10]. The other distances are comparable to those found in other systems [11].

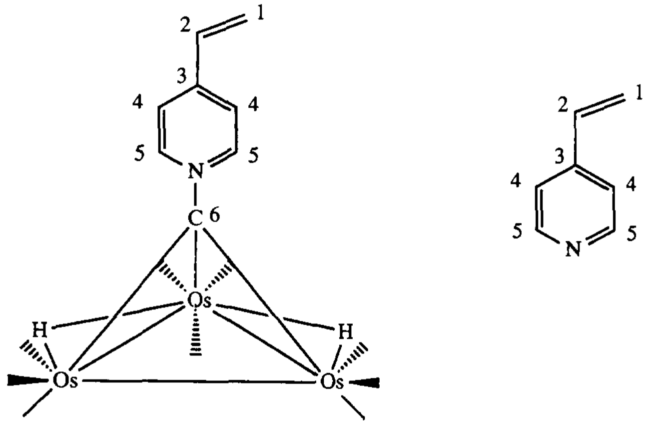


Fig. 1. The labelling schemes used for the assignments of $^{13}C\{^1H\}$ NMR spectra of 1 and the free ligand.

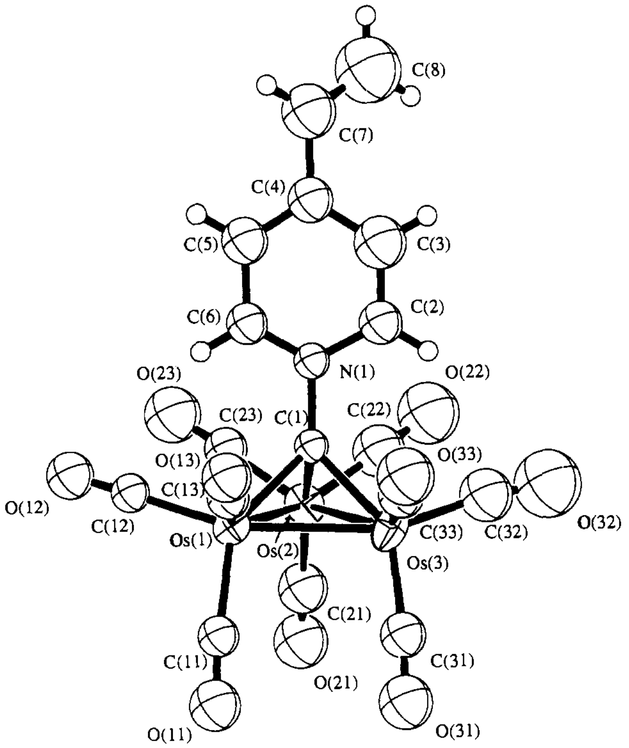


Fig. 2. The molecular structure of $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4\text{-}CH{=}CH_2)]$ (1).

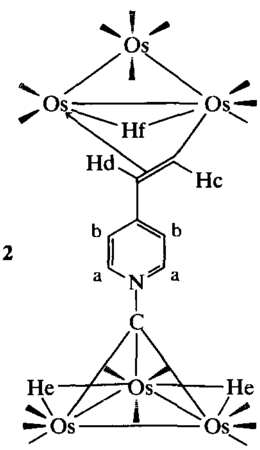
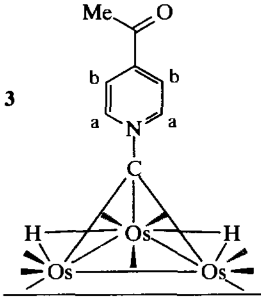
Treatment of the cluster 1 with a slight excess of the activated triosmium cluster $[Os_3(CO)_{10}(NCMe)_2]$ in refluxing n-hexane for 8 h produces a homonuclear-linked cluster $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4\text{-}\mu\text{-}\eta^2\text{-}CH{=}$

Table 2
Selected bond distances (Å) and bond angles (°) for $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4\text{-}CH{=}CH_2)]$ (1)

Os(1)–Os(2)	2.861(1)	Os(1)–Os(3)	2.758(1)
Os(2)–Os(3)	2.874(2)	Os(1)–C(1)	2.10(2)
Os(2)–C(1)	2.09(2)	Os(3)–C(1)	2.06(2)
N(1)–C(1)	1.48(3)	C(4)–C(7)	1.52(5)
C(7)–C(8)	1.40(10)		
Os(2)–Os(1)–Os(3)	61.48(4)	Os(1)–Os(2)–Os(3)	57.49(3)
Os(1)–Os(3)–Os(2)	61.03(4)	Os(1)–C(1)–Os(2)	85.9(9)
Os(1)–C(1)–Os(3)	83.3(8)	Os(2)–C(1)–Os(3)	87.8(8)
C(1)–N(1)–C(2)	119(2)	C(1)–N(1)–C(6)	119(2)
C(4)–C(7)–C(8)	121(5)		

CH)$Os_3(\mu$-H)(CO)$_{10}$] (**2**) in moderate yield (ca. 34%); **2** was characterised on the basis of its FAB mass spectrum, which shows the molecular ion at 1793 (simulated $m/z = 1793$). It is worth noting that the IR spectrum of **2** in the range 2150–1800 cm^{-1} appears to be a simple combination of that found for the constituent species, namely, [$Os_3(\mu$-$H)_2(CO)_9(\mu_3$-CNC_5H_4-CH=CH_2)] [3] and [$Os_3(\mu$-H)(CH=CHR)$(CO)_{10}$] (R = H, Me, Ph) [12]. In addition, the ^1H NMR spectrum of **2** shows features common to both species. The spectroscopic data for **2**, presented in Table 3, are consistent with the solid-state structure. The vinyl group in **2** is on a bridging mode because the spread of chemical shifts in its ^1H NMR spectrum is larger than that expected for a simple σ-bonded C_2H_2R group [13], and resembles that of a C_2H_2R group with a σ-bond to one metal atom and a monoalkene-metal interaction to another metal atom [14]. An X-ray structure determination of **2** was carried out on a single crystal obtained by evaporation of a solution of **2** in *n*-hexane/CH_2Cl_2 during 2 days at room temperature. The molecular structure of **2** together with the atom labelling scheme, is depicted in Fig. 3, and some important bond distances and bond angles are presented in Table 4. The structure of **2** involves a triosmium alkylidyne metal core, with the 4-vinylpyridine simultaneously bonded to the μ_3-bridging alkylidyne carbon atom C(1) and another triosmium cluster unit Os(4)–Os(5)–Os(6). The same structural features as noted for **1** are observed in the alkylidyne metal core of **2**. The alkene unit adopts a *trans*-configuration. For the other Os_3 triangle of **2**, all the Os–Os bonds are single, and all the carbonyls are terminal. The proton on the vinyl carbon C(8) is probably the source of the metal hydride. The vinyl group and the hydride both bridge the same Os(4)–Os(6) edge of the $Os_3(CO)_{10}$ cluster unit. This is consistent with the ^1H NMR data. The Os(4)–Os(6) distance [2.8467(7) Å] is shorter than the other two Os–Os bonds [2.9008(7) Å and 2.8714(7) Å]. The metal-carbon distances suggest that the vinyl group is σ-bonded to Os(6) and π-bonded to Os(4). The cluster valence electrons of both cluster units in **2** are 48, and the species are electron precise according to EAN rule. If the vinyl group is considered to donate two electrons in forming the π-bond, the Os(4)–H–Os(6) unit forms a two-electron three-centre bond. The vinyl group and the Os atom to which it is σ-bonded [Os(6)–C(8) = 2.11(1) Å] are coplanar to within 0.03 Å. It is noteworthy that the dihedral angle between the planes containing the Os(4)–Os(6) vector and the C(7)–C(8) vector is ca. 60°. This is consistent with the C(7)–C(8) length of 1.40(2) Å, slightly longer

Table 3
Spectroscopic data for compounds 2 and 3

Compound	IR (ν_{CO})(cm^{-1}) [a]	^1H NMR, δ (ppm) [b]	MS
2 	2109m, 2089m, 2066s, 2056s, 2025vs, 1983s, 1951m, 1935m	9.58 [d, 2H, J(HaHb) = 6.9 Hz, Ha] 8.32 [dd, 1H, J(HcHd) = 13.9 Hz, J(HcHf) = 2.0 Hz, Hc] 7.19 [d, 2H, J(HbHa) = 6.9 Hz, Hb] 4.92 [d, 1H, J(HdHc) = 13.9 Hz, Hd] − 18.60 [d, 1H, J(HfHc) = 2.0 Hz, Hf] − 18.92 [s, 2H, He]	1793 (1793) [c]
3 	2091m, 2057vs, 2026vs, 1985s, 1953m, 1937m, 1705m,br	9.82 [d, 2H, J(HaHb) = 7.1 Hz, Ha] 7.79 [d, 2H, J(HbHa) = 7.1 Hz, Hb] 2.66 [s, 3H, Me] − 18.78 [s, 2H, OsH]	963 (963) [d]

[a] CH_2Cl_2, [b] CD_2Cl_2, [c] Simulated value, [d] Based on ^{192}Os.

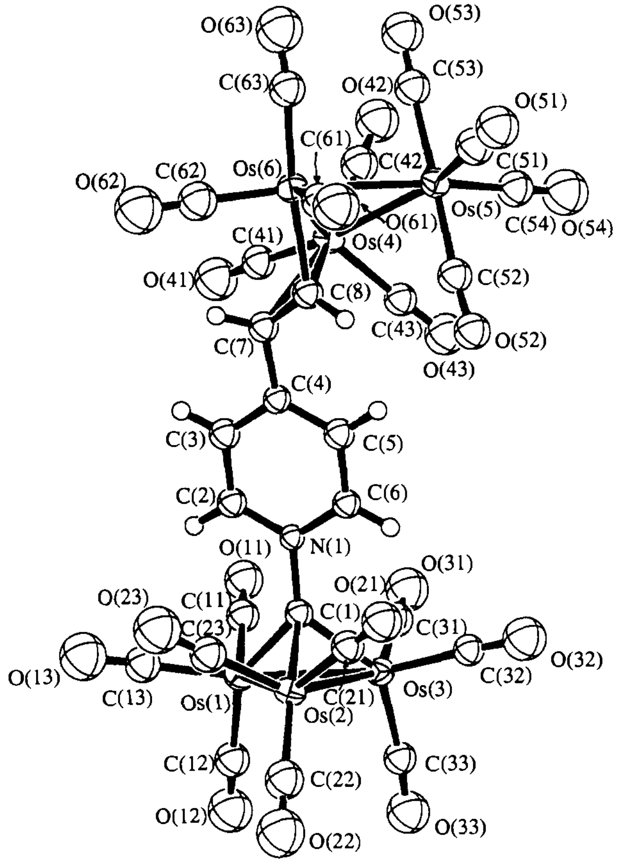


Fig. 3. The molecular structure of $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4\text{-}\mu\text{-}\eta^2\text{-}CH{=}CH_2)]\ Os_3(\mu\text{-}H)_2(CO)_{10}$ (**2**).

than the 1.34 Å expected for a C–C double bond. A similar bridging situation [15–18] has been encountered in $[Os_3(\mu\text{-}H)(CH{=}CH_2)(CO)_{10}]$ and its μ-but-1-enyl analogue [19], for the former of which combined X-ray and neutron diffraction studies were carried out [20].

The reaction of **1** with traces of water in the air using stoichiometric amounts of $RhCl(PPh_3)_3$ as catalyst leads to direct formation of an acyl alkylidyne cluster $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4\text{-}C(O)CH_3)]$ (**3**) (ca. 29% yield). Compound **3** was characterised by spectroscopic methods (Table 3). A broad IR absorption band at 1705 cm^{-1} indicates the presence of an acyl group [21], while the pattern of IR bands in the range 2150–1800 cm^{-1} is analogous to that of the related clusters $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CY)]$ (Y = Lewis base) [11]. Disappearance of the resonances from the vinyl group were observed in the ^1H NMR spectrum of **3**. Two sets of doublets and a strong methyl singlet from the acetyl group were observed. The signal at δ −18.78 indicates the presence of metal hydrides. Further confirmation of the presence of an acyl group comes from the mass spectrum of **3**. A molecular ion peak at 963 is observed in the FAB mass spectrum of **3**; it differs by 16 amu from that for **1**. It is likely that one oxygen atom is inserted into the vinyl group, with a corresponding hydrogen shift to give the methyl group. The reaction probably proceeds in an analogous manner to the Wacker process, and a detailed mechanistic study is under way. The formation of **3** from **1** involves the conversion of an alkene group into an acyl group, and this represents a versatile method for systematic functionalization of alkylidyne substituents on the trinuclear metal surface.

Table 4
Selected bond distances (Å) and bond angles (°) for $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4\text{-}\mu\text{-}\eta^2\text{-}CH{=}CH)Os_3(\mu\text{-}H)(CO)_{10}]$ (**2**)

Os(1)–Os(2)	2.8780(7)	Os(1)–Os(3)	2.7564(7)
Os(2)–Os(3)	2.8858(7)	Os(4)–Os(5)	2.9008(7)
Os(4)–Os(6)	2.8467(7)	Os(5)–Os(6)	2.8714(7)
Os(1)–C(1)	2.06(1)	Os(2)–C(1)	2.10(1)
Os(3)–C(1)	2.08(2)	N(1)–C(1)	1.49(1)
C(4)–C(7)	1.51(2)	C(7)–C(8)	1.40(2)
Os(4)–C(7)	2.38(1)	Os(4)–C(8)	2.29(1)
Os(6)–C(8)	2.11(1)		
Os(2)–Os(1)–Os(3)	61.57(2)	Os(1)–Os(2)–Os(3)	57.14(2)
Os(1)–Os(3)–Os(2)	61.29(2)	Os(5)–Os(4)–Os(6)	59.94(2)
Os(4)–Os(5)–Os(6)	59.10(2)	Os(4)–Os(6)–Os(5)	60.97(2)
Os(1)–C(1)–Os(2)	87.5(5)	Os(1)–C(1)–Os(3)	83.5(4)
Os(2)–C(1)–Os(3)	87.3(5)	C(1)–N(1)–C(2)	121(1)
C(1)–N(1)–C(6)	119.1(9)	C(4)–C(7)–C(8)	123(1)
Os(6)–C(8)–C(7)	122.0(9)	Os(4)–Os(6)–C(8)	52.6(4)
Os(4)–C(8)–C(7)	76.3(8)	Os(4)–C(7)–C(8)	69.1(8)
Os(4)–C(8)–Os(6)	80.4(5)		

Table 5
Selected bond distances (Å) and bond angles (°) for $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4\text{-}C(O)CH_3)]$ (**3**)

	molecule 1	molecule 2		molecule 1	molecule 2
Os(1)–Os(2)	2.864(1)	2.879(1)	Os(1)–Os(3)	2.873(1)	2.871(2)
Os(2)–Os(3)	2.766(2)	2.759(2)	Os(1)–C(1)	2.20(2)	2.02(2)
Os(2)–C(1)	2.02(3)	2.15(2)	Os(3)–C(1)	2.10(3)	2.05(2)
N(1)–C(1)	1.44(3)	1.44(3)	C(2)–C(73)	1.54(4)	1.54(4)
O(1)–C(2)	1.21(4)	1.17(3)	C(2)–C(3)	1.46(4)	1.48(4)
	molecule 1	molecule 2		molecule 1	molecule 2
Os(2)–Os(1)–Os(3)	57.64(4)	57.36(3)	Os(1)–Os(2)–Os(3)	61.34(4)	61.17(4)
Os(1)–Os(3)–Os(2)	61.02(4)	61.47(3)	Os(1)–C(1)–Os(2)	85.4(9)	87.3(9)
Os(1)–C(1)–Os(3)	83.9(9)	89.7(10)	Os(2)–C(1)–Os(3)	84.2(10)	82.2(9)
C(1)–N(1)–C(75)	121(2)	122(2)	C(1)–N(1)–C(71)	123(2)	121(2)
O(1)–C(2)–C(73)	117(2)	120(2)	O(1)–C(2)–C(3)	123(3)	126(3)

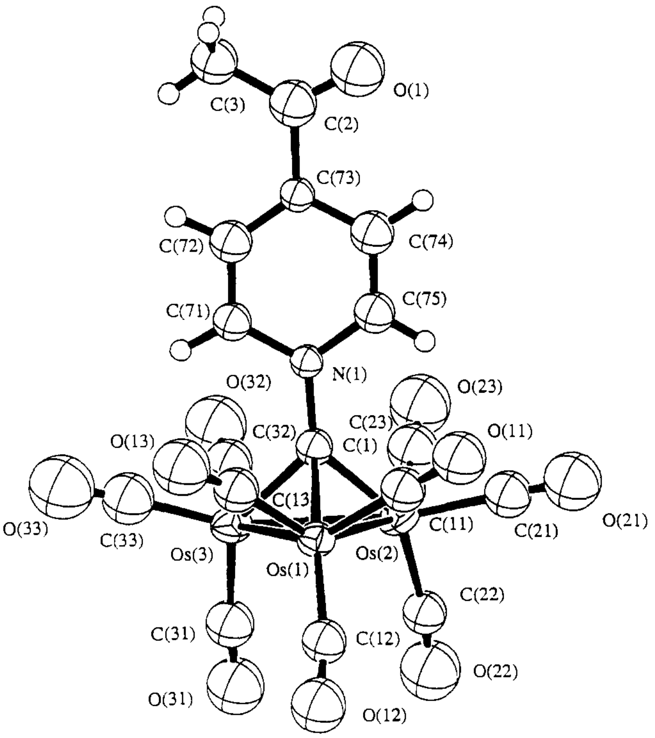


Fig. 4.The molecular structure of $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4\text{-}C(O)CH_3)]$ (3).

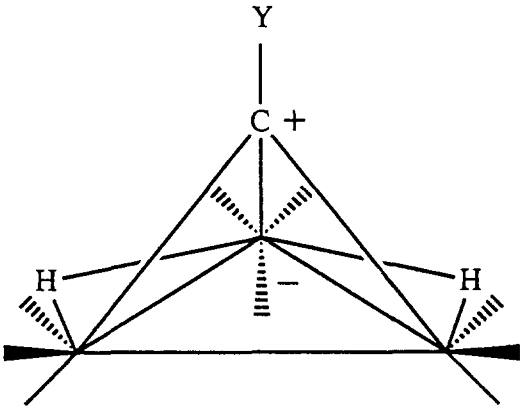


Fig. 5. The zwitterionic formulation for 1–3.

The molecular geometry of 3 was established by an X-ray diffraction study on a crystal obtained by evaporation of a solution of 3 in n-hexane/CH_2Cl_2 during 3 day at room temperature. A perspective view of the molecular structure of 3 together with the atom labelling scheme is depicted in Fig. 4, and some important bond distances and bond angles are listed in Table 5. There are two independent molecules in the asymmetric unit of 3, and the structure of 3 also involves a triosmium alkylidyne metal core, with the 4-acetylpyridine bonded to the apical carbon C(1). Potential energy calculations revealed that the two hydrides separately bridge the Os(1)–Os(2) and Os(1)–Os(3) edges [Os(1)–Os(2) = 2.864(1) Å and Os(1)–Os(3) = 2.873(1) Å]. The O(1)–C(2) distance [1.21(4) Å] is typical of an acyl C=O group, and the angles O(1)–C(2)–C(73) and O(1)–C(2)–C(3) are close to 120° [117(2)° and 123(3)°, respectively].

All three complexes can best be described by a charge-separated zwitterionic formulation, analogous to that for N-alkylated heterocycles, and hence may be represented as shown in Fig. 5. IR spectroscopy offers an ideal method for confirming this charge separation. The solution IR spectra of 1–3 show unusually low carbonyl-stretching frequencies for neutral clusters. The observation that protonation by CF_3COOH or HBF_4 preferentially occurs at the metal framework rather than at the organic fragment offers further evidence for the electron-withdrawing nature of the "Os_3C" core. As mentioned before, the upfield ^{13}C resonance for the methylidyne carbon in 1 suggests an excess of electron density within the inorganic moiety.

The deep colour in the solid state displayed by 1–3 prompted us to examine them by optical spectroscopy. Fenske-Hall molecular orbital calculations on these

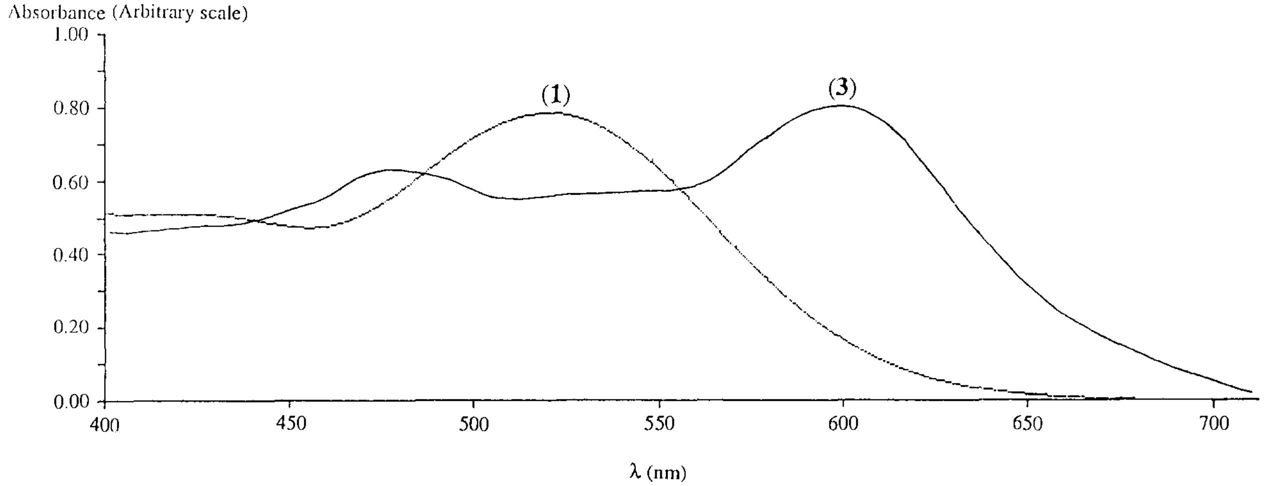


Fig. 6. The UV/VIS spectra of 1 and 3 in CH_2Cl_2.

Table 6
Optical spectral parameters for the compounds **1–3**

	Solvent	Colour	λ_{max} (nm)	$10^{-3}\varepsilon$ ($dm^3\ mol^{-1}\ cm^{-1}$)
1	*n*-hexane	violet	570	4.8
	carbon tetrachloride	purple	561	4.1
	dichloromethane	red	520	4.3
	acetone	orange	492	4.3
2 [a]	carbon tetrachloride	blue	601	6.1
	dichloromethane	purple	558	5.7
	acetone	orange	491	6.9
3	*n*-hexane	green	637	4.2
	carbon tetrachloride	green	627	6.2
	dichloromethane	blue	590	5.1
	acetone	red	537	4.0

[a] Limited solubility in *n*-hexane.

compounds revealed that the highest occupied molecular orbital (HOMO) is largely metal-based, and the lowest unoccupied molecular orbital (LUMO) mostly based on the organic moiety [22]. The intense colour arises from a strong absorption because of a metal-to-ligand charge-transfer (M.L.C.T.) transition. The study of complexes **1–3** in a variety of organic solvents by UV/VIS spectroscopy showed that they exhibit exceptionally large negative solvatochromism (hypsochromic shift) which extends over almost the whole visible range. That is, the M.L.C.T. absorption blue shifts in progressively more polar solvent media, ($\mu_g > \mu_e$), where μ_g and μ_e are the dipole moments in the ground state and the excited state, respectively [23]. This behaviour is in direct contrast to the positive solvatochromism shown by bithiophene [24]. The optical spectral data for **1–3** in a range of solvents are summarised in Table 6. One important feature is that a large difference in λmax for **1** and **3** in the same solvent was observed (Fig. 6). The electron-withdrawing ability of the COMe group in **3** substantially reduces the dipole moment of **3** in the ground state and this hence results in a lower transition energy (longer λmax). The observation of such solvatochromic behaviour for these complexes may provide a good opportunity for the development of new

Table 7
Crystal data and data collection parameters for **1–3**

Compound	1	2	3
Formula	$Os_3C_{17}H_9NO_9$	$Os_6C_{27}H_9NO_{19}$	$Os_3C_{17}H_9NO_{10}$
Formula weight	941.6	1792.2	957.6
Colour, habit	Red blocks	Purple rods	Red plates
Crystal dimensions (mm)	0.20 × 0.32 × 0.40	0.18 × 0.20 × 0.38	0.04 × 0.16 × 0.28
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)	$P2_1$ (No. 4)
a (Å)	11.017(4)	11.872(2)	8.517(1)
b (Å)	11.048(6)	12.460(4)	23.448(2)
c (Å)	17.862(9)	12.696(5)	11.055(2)
α (°)	90.0	95.21(3)	90.0
β (°)	90.0	96.97(2)	91.38(2)
γ (°)	90.0	92.73(2)	90.0
V (Å^3)	2173(2)	1853(2)	2207.2(5)
Z	4	2	4
D_{calc} (g cm^{-3})	2.878	3.212	2.881
μ(Mo Kα) (cm^{-1})	175.72	205.99	173.05
F(000)	1672	1572	1704
Temperature (K)	296	296	298
Scan type	ω–2θ	ω–2θ	ω–2θ
Scan rate in ω (deg min^{-1})	1.24–8.24	1.24–8.24	16.0
Scan range (°)	0.60 + 0.34 tan θ	0.45 + 0.34 tan θ	1.10 + 0.35 tan θ
2θ range (°)	2–45	2–45	2–45
Reflections collected	1667	5123	3201
Unique reflections	1667	4555	2976
Observed reflections [$F > n\sigma(F)$]	1466 (n = 3)	4167 (n = 3)	2651 (n = 6)
Absorption correction	Psi-scans	Psi-scans	Psi-scans
Transmission factors	0.635–0.991	0.353–0.999	0.4434–1.0000
Weighting scheme $\omega = [\sigma^2(F^2) + gF^2]^{-1}$	g = 0.04	g = 0.04	g = 0.005
R	0.041	0.035	0.032
R_w	0.053	0.048	0.035
Residual electron density (e Å^{-3}) (close to Os)	1.31 to −1.41	1.20 to −1.35	1.20 to −0.78

materials for non-linear optics, and a good system for solvent polarity correlation [25,26].

3. Experimental details

3.1. Materials and methods

None of the compounds reported is particularly air sensitive, but all reactions were carried out under dry dinitrogen using standard Schlenk and vacuum line techniques. Dichloromethane was dried over CaH_2 and *n*-hexane was distilled from sodium benzophenone ketyl. Chemicals, except where stated, were purchased from commercial sources and used as received. The compounds $[Os_3(\mu\text{-H})_3(CO)_9(\mu_3\text{-CCl})]$ [27] and $[Os_3(CO)_{10}(NCMe)_2]$ [28] were prepared by published

Table 8
Atomic coordinates and isotropic displacement coefficients B_{eq} (Å^2) for $[Os_3(\mu\text{-H})_2(CO)_9(\mu_3\text{-CNC}_5H_4\text{-CH=CH}_2)]$ (**1**)

Atom	*x*	*y*	*z*	B_{eq}
Os1	0.45843(8)	0.10654(8)	0.01364(6)	3.18(2)
Os2	0.5186(1)	−0.14538(9)	0.01123(6)	3.58(2)
Os3	0.3620(1)	−0.4166(9)	0.12275(6)	4.08(2)
O11	0.215(2)	0.140(2)	−0.074(1)	6.5(5) *
O12	0.643(2)	0.212(2)	−0.091(1)	5.6(4) *
O13	0.440(2)	0.333(2)	0.110(1)	6.1(5) *
O21	0.395(2)	−0.296(2)	−0.108(1)	7.4(6) *
O22	0.613(3)	−0.360(2)	0.105(1)	9.6(7) *
O23	0.757(2)	−0.107(2)	−0.069(1)	7.9(6) *
O31	0.097(2)	−0.015(2)	0.069(1)	7.3(5) *
O32	0.351(3)	−0.240(3)	0.236(2)	11.5(9) *
O33	0.337(2)	0.161(2)	0.234(1)	8.3(6) *
N1	0.650(2)	0.008(2)	0.138(1)	3.2(4) *
C1	0.539(2)	−0.010(2)	0.092(1)	2.9(4) *
C2	0.658(2)	−0.047(2)	0.207(2)	4.7(6) *
C3	0.765(3)	−0.035(3)	0.247(2)	6.9(9) *
C4	0.864(3)	0.032(2)	0.219(2)	5.1(6) *
C5	0.850(3)	0.087(3)	0.152(2)	5.4(6) *
C6	0.738(2)	0.074(2)	0.112(1)	4.3(5) *
C7	0.984(3)	0.041(3)	0.261(2)	7.4(9) *
C11	0.311(2)	0.130(2)	−0.042(1)	4.2(5) *
C12	0.576(2)	0.172(2)	−0.051(1)	3.8(5) *
C13	0.444(2)	0.249(2)	0.073(2)	4.4(6) *
C21	0.444(3)	−0.242(3)	−0.063(2)	6.1(7) *
C22	0.572(3)	−0.271(3)	0.068(2)	6.8(8) *
C23	0.666(2)	−0.128(2)	−0.038(2)	4.6(6) *
C31	0.198(3)	−0.030(3)	0.092(2)	5.2(6) *
C32	0.362(3)	−0.159(3)	0.196(2)	7.0(8) *
C33	0.349(3)	0.078(3)	0.192(2)	5.2(6) *
C8	1.021(8)	−0.050(8)	0.309(5)	11(3) *
C8A	1.069(7)	0.132(7)	0.256(4)	9(2) *

Starred atoms were refined isotropically.
Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
$(4/3) * [a^2 * B(1, 1) + b^2 * B(2, 2) + c^2 * B(3, 3) + ab(\cos\gamma) * B(1, 2) + ac(\cos\beta) * B(1, 3) + bc(\cos\alpha) * B(2, 3)]$.

Table 9
Atomic coordinates and isotropic displacement coefficients B_{eq} (Å^2) for $[Os_3(\mu\text{-H})_2(CO)_9(\mu_3\text{-CNC}_5H_4\text{-}\mu\text{-}\eta^2\text{-CH=CH})Os_3(\mu\text{-H})(CO)_{10}]$ (**2**)

Atom	*x*	*y*	*z*	B_{eq}
Os1	0.19394(4)	0.15691(4)	0.30291(4)	2.43(1)
Os2	0.33869(4)	−0.00672(4)	0.23253(4)	2.53(1)
Os3	0.28739(4)	0.02527(4)	0.44921(4)	2.43(1)
Os4	−0.28144(4)	−0.40738(4)	0.24397(4)	2.50(1)
Os5	−0.23353(5)	−0.62974(4)	0.27261(4)	2.79(1)
Os6	−0.28319(5)	−0.56062(4)	0.06316(4)	2.70(1)
O11	−0.0162(9)	0.1881(9)	0.4119(8)	4.5(2) *
O12	0.312(1)	0.375(1)	0.4005(9)	5.9(3) *
O13	0.090(1)	0.231(1)	0.091(1)	6.9(3) *
O21	0.371(1)	−0.2471(9)	0.2246(8)	4.9(2) *
O22	0.574(1)	0.058(1)	0.174(1)	7.1(3) *
O23	0.215(1)	−0.023(1)	0.007(1)	6.9(3) *
O31	0.104(1)	0.060(1)	0.5939(9)	5.5(3) *
O32	0.366(1)	−0.169(1)	0.5601(9)	5.7(3) *
O33	0.446(1)	0.206(1)	0.5760(9)	5.5(3) *
O41	−0.363(1)	−0.184(1)	0.2161(9)	5.5(3) *
O42	−0.475(1)	−0.459(1)	0.3716(9)	5.6(3) *
O43	−0.117(1)	−0.3549(9)	0.4486(9)	5.2(2) *
O51	−0.182(1)	−0.861(1)	0.2080(9)	5.5(3) *
O52	0.024(1)	−0.571(1)	0.2933(9)	6.1(3) *
O53	−0.490(1)	−0.6941(9)	0.2547(8)	5.3(2) *
O54	−0.203(1)	−0.628(1)	0.515(1)	6.4(3) *
O61	−0.133(1)	−0.724(1)	−0.024(1)	6.5(3) *
O62	−0.325(1)	−0.455(1)	−0.144(1)	7.0(3) *
O63	−0.493(1)	−0.717(1)	0.007(1)	6.6(3) *
N1	0.0920(8)	−0.0912(8)	0.2649(7)	1.9(2) *
C1	0.187(1)	−0.009(1)	0.3029(9)	2.4(2) *
C2	0.003(1)	−0.069(1)	0.1963(9)	2.6(2) *
C3	−0.079(1)	−0.145(1)	0.154(1)	2.8(2) *
C4	−0.073(1)	−0.252(1)	0.1798(9)	2.4(2) *
C5	0.016(1)	−0.275(1)	0.2521(9)	2.8(2) *
C6	0.099(1)	−0.193(1)	0.2953(9)	2.4(2) *
C7	−0.163(1)	−0.335(1)	0.126(1)	2.8(2) *
C8	−0.151(1)	−0.446(1)	0.129(1)	2.8(2) *
C11	0.064(1)	0.173(1)	0.369(1)	3.2(3) *
C12	0.268(1)	0.292(1)	0.361(1)	3.6(3) *
C13	0.130(1)	0.204(1)	0.174(1)	3.9(3) *
C21	0.357(1)	−0.157(1)	0.229(1)	3.3(3) *
C22	0.487(1)	0.032(1)	0.195(1)	4.6(3) *
C23	0.266(1)	−0.019(1)	0.090(1)	3.9(3) *
C31	0.173(1)	0.044(1)	0.534(1)	3.6(3) *
C32	0.335(1)	−0.097(1)	0.516(1)	2.9(2) *
C33	0.387(1)	0.134(1)	0.530(1)	3.1(3) *
C41	−0.335(1)	−0.270(1)	0.226(1)	3.4(3) *
C42	−0.402(1)	−0.442(1)	0.322(1)	4.1(3) *
C43	−0.180(1)	−0.371(1)	0.373(1)	3.2(3) *
C51	−0.203(1)	−0.776(1)	0.233(1)	4.2(3) *
C52	−0.075(1)	−0.590(1)	0.282(1)	3.6(3) *
C53	−0.397(1)	−0.669(1)	0.259(1)	3.8(3) *
C54	−0.216(1)	−0.627(1)	0.424(1)	3.9(3) *
C61	−0.188(1)	−0.661(1)	0.009(1)	3.8(3) *
C62	−0.311(1)	−0.494(1)	−0.063(1)	4.6(3) *
C63	−0.414(1)	−0.657(1)	0.031(1)	3.9(3) *

Starred atoms were refined isotropically.
Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) * [a2 * B(1, 1) + b2 * B(2, 2) + c2 * B(3, 3) + ab(\cos\gamma) * B(1, 2) + ac(\cos\beta) * B(1, 3) + bc(\cos\alpha) * B(2, 3)]$.

Table 10
Atomic coordinates and isotropic displacement coefficients B_{eq} (Å^2) for $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4\text{–}C(O)CH_3)]$ (**3**)

Atom	x	y	z	B_{eq}
Os(1)	0.1986(1)	0.3174	0.19632(10)	2.97(2)
Os(2)	0.2413(1)	0.43151(6)	0.1105(1)	3.51(3)
Os(3)	−0.0410(1)	0.37725(6)	0.0600(1)	3.40(2)
Os(4)	0.3550(1)	0.11799(5)	0.57703(10)	3.14(2)
Os(5)	0.5878(1)	0.19983(6)	0.5773(1)	3.52(3)
Os(6)	0.2954(1)	0.2267	0.6879(1)	3.20(2)
O(1)	−0.064(3)	0.4995(10)	0.746(2)	6.6(6)
O(2)	0.595(3)	0.069(1)	1.255(2)	6.6(6)
O(11)	0.436(3)	0.3438(10)	0.403(2)	6.3(5)
O(12)	0.359(3)	0.222(1)	0.068(2)	6.8(6)
O(13)	−0.024(3)	0.246(1)	0.340(2)	7.2(6)
O(21)	0.544(3)	0.468(1)	0.244(2)	7.8(7)
O(22)	0.343(3)	0.444(1)	−0.153(3)	8.1(7)
O(23)	0.113(3)	0.559(1)	0.113(3)	8.2(7)
O(31)	0.029(3)	0.370(1)	−0.205(2)	7.2(6)
O(32)	−0.225(3)	0.491(1)	0.034(3)	8.2(7)
O(33)	−0.330(3)	0.313(1)	0.106(3)	9.3(8)
O(41)	0.589(3)	0.028(1)	0.541(2)	6.4(5)
O(42)	0.125(2)	0.0430(9)	0.689(2)	5.6(5)
O(43)	0.249(3)	0.129(1)	0.310(2)	6.9(6)
O(51)	0.870(3)	0.124(1)	0.576(3)	8.7(7)
O(52)	0.589(3)	0.2203(10)	0.298(2)	6.1(5)
O(53)	0.772(4)	0.307(1)	0.668(3)	10.6(9)
O(61)	0.093(3)	0.321(1)	0.551(2)	6.5(5)
O(62)	0.448(3)	0.318(1)	0.857(2)	7.3(6)
O(63)	0.055(3)	0.196(1)	0.868(2)	7.2(6)
N(1)	0.015(2)	0.4169(8)	0.336(2)	2.4(4)
N(2)	0.520(2)	0.1487(8)	0.836(2)	3.0(4)
C(1)	0.078(3)	0.399(1)	0.222(2)	3.1(5)
C(2)	−0.157(4)	0.474(1)	0.681(3)	5.0(7)
C(3)	−0.318(4)	0.461(1)	0.716(3)	4.7(7)
C(4)	0.464(3)	0.168(1)	0.719(2)	2.8(5)
C(5)	0.678(4)	0.097(1)	1.197(3)	5.0(7)
C(6)	0.844(4)	0.112(2)	1.226(3)	7.0(9)
C(11)	0.343(3)	0.333(1)	0.325(3)	4.5(6)
C(12)	0.309(3)	0.261(1)	0.119(3)	4.4(6)
C(13)	0.061(3)	0.277(1)	0.290(3)	4.5(6)
C(21)	0.431(4)	0.454(1)	0.195(3)	5.0(7)
C(22)	0.317(3)	0.441(1)	−0.051(3)	4.3(6)
C(23)	0.164(4)	0.511(2)	0.109(3)	5.7(8)
C(31)	−0.005(4)	0.372(1)	−0.104(3)	5.1(7)
C(32)	−0.141(3)	0.449(1)	0.050(3)	4.8(7)
C(33)	−0.219(4)	0.339(2)	0.093(3)	6.1(8)
C(41)	0.499(4)	0.065(1)	0.553(3)	5.3(7)
C(42)	0.207(3)	0.0760(10)	0.651(2)	2.6(5)
C(43)	0.290(3)	0.123(1)	0.413(3)	4.5(6)
C(51)	0.756(4)	0.154(2)	0.573(3)	6.3(8)
C(52)	0.587(4)	0.216(1)	0.403(3)	5.5(7)
C(53)	0.714(6)	0.259(2)	0.630(5)	11(1)
C(61)	0.171(4)	0.288(2)	0.608(3)	6.1(8)
C(62)	0.389(4)	0.286(1)	0.788(3)	5.5(7)
C(63)	0.144(4)	0.209(1)	0.802(3)	4.6(6)
C(71)	−0.136(3)	0.405(1)	0.369(2)	3.2(5)
C(72)	−0.186(3)	0.423(1)	0.477(3)	4.0(6)
C(73)	−0.099(3)	0.4534(10)	0.558(2)	2.7(5)
C(74)	0.055(3)	0.464(1)	0.530(3)	4.3(6)
C(75)	0.107(3)	0.446(1)	0.423(3)	3.7(6)
C(81)	0.443(3)	0.107(1)	0.902(2)	3.4(5)
C(82)	0.502(3)	0.093(1)	1.011(3)	3.7(5)
C(83)	0.628(3)	0.116(1)	1.068(3)	3.8(5)
C(84)	0.706(3)	0.157(1)	1.007(3)	4.1(6)
C(85)	0.651(3)	0.174(1)	0.894(2)	3.2(5)

methods. The synthesis of $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4\text{–}CH{=}CH_2)]$ (**1**) was recently reported [3].

IR spectra were recorded on a BIO-RAD FTS-7 IR spectrometer using 0.5 mm solution cells. The ^1H NMR spectra were recorded on a JEOL GSX 270FT-NMR spectrometer using deuteriated solvents as lock and reference [$SiMe_4(\delta = 0)$]. Mass spectra (FAB) were recorded on a Finnigan MAT 95 instrument. Electronic absorption spectra were obtained with a microprocessor-controlled Perkin Elmer UV/VIS spectrophotometer Lambda 3B, thermostatted by use of a Lauda circulating bath. Products were separated in air by thin-layer chromatography on plates coated with Merck Kieselgel 60 GF_{254}.

3.2. *Synthesis of $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4\text{-}\mu\text{-}\eta^2\text{-}CH{=}CH)Os_3(\mu\text{-}H)(CO)_{10}]$ (2)*

A slight excess of $[Os_3(CO)_{10}(NCMe)_2]$ (75 mg, 0.08 mmol) in CH_2Cl_2 (10 ml) was added to a solution of $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4\text{–}CH{=}CH_2)]$ (**1**) (50 mg, 0.05 mmol) in *n*-hexane (30 ml). The solution was refluxed at 60° for 8 h, at which point the colour had turned to dark purple. The solvent was then removed under vacuo, and the residue was subjected to preparative TLC with *n*-hexane/CH_2Cl_2 (85 : 15, v/v) as eluant. A small amount of **1** (8 mg, 0.008 mmol, 16%) was recovered from the second red band. No attempt was made to identify the first yellow band because of its impure character. Crystallisation of the product from the deep-purple band in *n*-hexane/CH_2Cl_2 produced air-stable, purple needles of **2** (32 mg, 0.018 mmol, 34%).

3.3. *Synthesis of $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4\text{–}C(O)CH_3)]$ (3)*

To a solution of **1** (50 mg, 0.05 mmol) in dichloromethane (30 ml) were added, a slight excess of Wilkinson's catalyst (74 mg, 0.08 mmol) and traces of water (three drops). The mixture was stirred under reflux in air for 8 h. The solvent was removed under vacuo. Purification by TLC with *n*-hexane/CH_2Cl_2 (75 : 25, v/v) as eluant afforded a single major product. The first, red, band gave the starting material **1** (15 mg, 0.016 mmol, 30%) and the second, blue, band gave $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4\text{-}C(O)CH_3)]$ (**3**) (15 mg, 0.016 mmol, 29%).

3.4. *X-Ray Analyses of compounds 1–3*

For structures **1** and **2**, intensity data were collected on an Enraf-Nonius CAD4 diffractometer, while for structure **3**, data were recorded on a Rigaku AFC7R diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) in both cases. For all the structures, the intensity data were corrected for Lorentz polarisation effects and for absorption by the Ψ-scan method. The crystal data and data collection details for **1–3** are summarised in Table 7. The structures were solved by a combination of direct methods and Fourier difference techniques, and refined on F by full-matrix least-squares analysis (using the SDP program for **1** and **2** [29]; TeXsan for **3** [30]) until convergence was reached. Positional disorder for C(8) was encountered in the case of **1**. A two site model for C(8), with occupancy factor 0.5 for each, was used in the refinement to give a satisfactory result. The hydrogen atoms of the organic moieties were placed in their positions (C–H, 0.96 Å). The positions of the hydride atoms were estimated from potential energy calculations [9]. Final atomic coordinates for the three structures are presented in Tables 8–10. Tables of hydrogen atom coordinates and thermal parameters, and complete lists of bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre.

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