

Preliminary Communication

Synthesis of novel triosmium alkylidene carbonyl clusters. Crystal structures of $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-CNC}_5\text{H}_4\text{-CH=CH}_2)]$ and $[\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu\text{-C(H)NC}_5\text{H}_4\text{-}\eta^2\text{-CH=CH}_2)]$

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Abstract

The neutral cluster $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-CNC}_5\text{H}_4\text{-CH=CH}_2)]$ (**1**) has been made in good yield by the reaction of $[\text{Os}_3(\mu\text{-H})_3(\text{CO})_9(\mu_3\text{-CCl})]$ and 2-vinylpyridine in the presence of an excess of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene). Thermolysis of **1** in n-hexane gives a novel triosmium alkylidene cluster $[\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu\text{-C(H)NC}_5\text{H}_4\text{-}\eta^2\text{-CH=CH}_2)]$ (**2**). Both complexes have been fully characterised by spectroscopic methods and their structures established by X-ray crystallography.

Key words: Osmium; Cluster; Carbonyl; Alkylidene; Crystal structure

We have reported the preparation of some triosmium alkylidene [1] and triruthenium alkylidene [2] clusters bearing nitrogen substituents such as pyridine, quinoline and isoquinoline on the apical carbon atom. When we extended this work to substituted pyridines, the new cluster $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-CNC}_5\text{H}_4\text{-CH=CH}_2)]$ (**1**) was obtained. Heating complex (**1**) in n-hexane led to a new alkylidene cluster $[\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu\text{-C(H)NC}_5\text{H}_4\text{-}\eta^2\text{-CH=CH}_2)]$ (**2**).

The reaction of $[\text{Os}_3(\mu\text{-H})_3(\text{CO})_9(\mu_3\text{-CCl})]$ with 1 equivalent of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), in the presence of a 10-fold excess of 2-vinylpyridine gave the red-purple product **1** in 66% yield, see Scheme 1. (The sterically hindered base DBU acts as a deprotonating agent for the metal cluster. A proposed mechanism for this type of reaction has been suggested [1]. In the absence of DBU, no reaction is observed.) When a solution of complex **1** in n-hexane was refluxed

at 60°C for 3 h, the mixture turned from deep purple to orange. A new compound **2** was isolated from an orange-yellow band (30% yield) after chromatography on silica (t.l.c.) with n-hexane/CH₂Cl₂ (80:20) as eluent (see Scheme 1). A few minor products remain unidentified.

The spectroscopic data (IR, ¹H NMR and MS) for the new clusters **1** and **2** are summarised in Table 1. The proton signals owing to the organic moieties are fully consistent with the solid-state structures. Attempts to assign all the signals for **2** were made with the aid of double resonance experiments. Irradiation of the signal at δ -15.75 ppm collapsed the signal at δ 7.13 ppm to a singlet and the signal at δ 4.37 ppm to a simple triplet. When irradiation was at δ 4.37 ppm, the hydride signal appeared as a doublet and the signals at δ 3.50 ppm and δ 2.30 ppm collapsed to two singlets. Similarly, the signal at δ 7.24 ppm collapsed to a doublet of doublet upon irradiation at δ 8.46 ppm.

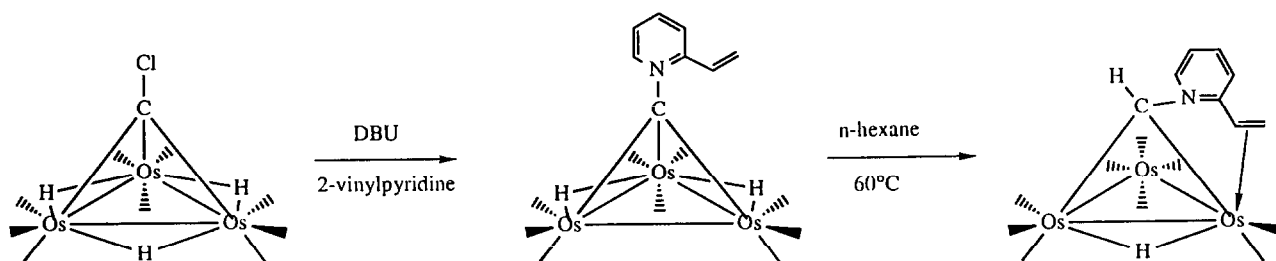
The molecular structures of both complexes **1** and **2** were established by X-ray diffraction studies [3*,4*]. Single crystals of both **1** and **2** were obtained from slow evaporation of an n-hexane/CH₂Cl₂ solution of **1** and **2** respectively at 0°C. Their molecular structures are shown in Figs. 1 and 2, respectively, together with some important bond parameters.

The molecular structure of **1** consists of a triosmium alkylidene metal core with the 2-vinylpyridine moiety bonded to the μ_3 -bridging alkylidene carbon atom. No bonding interaction between the alkene group and the metal atom(s) is observed. The two hydride atoms that show up in the ¹H NMR spectrum could not be located. However, potential energy calculations suggested that one hydride atom bridges the Os(1)–Os(3) edge and the other bridges the Os(2)–Os(3) edge [5]. These two edges (2.8622(7) and 2.8813(7)Å, respectively) are significantly longer than the Os(1)–Os(2) bond (2.7478(7)Å). This is consistent with the general observation that M–M bond length increases when the corresponding bond is bridged by a hydride atom [6].

The molecular structure of **2** also consists of a triosmium metal core with one Os–Os edge bridged by a hydride ligand and an alkylidene unit. This dibridged Os–Os bond [2.8057(7)Å] is significantly shorter than

* Reference number with an asterisk indicates a note in the list of references.

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Scheme 1.

the unbridged Os–Os bonds (Os(1)–Os(2), 2.8617(8)Å and Os(1)–Os(3), 2.8470(7)Å). This agrees with the general observation that there is a net shortening of the M–M distance in an M(μ -H)(μ -C)M system. Similar behaviour has previously been observed for [Os₃(μ -H)(CO)₁₀(C(H)CH₂PMe₂Ph)] [7].

Thermal treatment of 1 led to cleavage of one Os–C(alkylidene) bond, resulting in the formation of a μ -alkylidene ligand and hydride migration [8] from the Os–Os bond to the corresponding carbon atom C(1). Carbonyl ligand scrambling also takes place in this thermal transformation. Unlike the starting complex 1,

TABLE 1. Spectroscopic data for new compounds

Compounds	IR (ν_{CO})(cm^{-1}) ^a	¹ H NMR, δ (ppm) ^b	MS ^c
1	2022vs, 1982s, 1950m, 1934m	2089m, 2054vs, $J(\text{HaHc}) = 1.0$ Hz, Ha] 8.14 [1H, m, Hc] 7.98 [1H, dd, $J(\text{HgHe}) = 17.3$ Hz, $J(\text{HgHf}) = 11.2$ Hz, Hg] 7.58 [1H, dd, $J(\text{HdHc}) = 8.1$ Hz, $J(\text{HdHb}) = 1.5$ Hz, Hd] 7.34 [1H, m, Hb] 6.11 [1H, d, $J(\text{HeHg}) = 17.3$ Hz, He] 5.96 [1H, d, $J(\text{HfHg}) = 11.2$ Hz, Hf] –18.75 [2H, s, OsH]	10.24 [1H, dd, $J(\text{HaHb}) = 6.6$ Hz, 947 (947)
2	2087s, 2037vs, 1999vs, 1968vw, 1953m, 1939sh	8.46 [1H, d $J(\text{HaHb}) = 6.4$ Hz, Ha] 7.56 [2H, m, Hc and Hd] 7.24 [1H, m, Hb] 7.13 [1H, d, $J(\text{HhHi}) = 2.5$ Hz, Hh] 4.37 [1H, dt, $J(\text{HgHi}) = 2.5$ Hz, $J(\text{HgHe}) = J(\text{HgHf}) = 8.5$ Hz, Hg] 3.50 [1H, dd, $J(\text{HeHg}) = J(\text{HfHg}) = 8.5$ Hz, $J(\text{HeHf}) = 2.0$ Hz, He or Hf] 2.30 [1H, dd, $J(\text{HeHg}) = J(\text{HfHg}) = 8.5$ Hz, $J(\text{HeHf}) = 2.0$ Hz, He or Hf] –15.75 [1H, t, $J(\text{HiHh}) = J(\text{HiHg}) = 2.5$ Hz, Hi]	947 (947)

^a CH₂Cl₂; ^b CD₂Cl₂; ^c base on ¹⁹²Os.

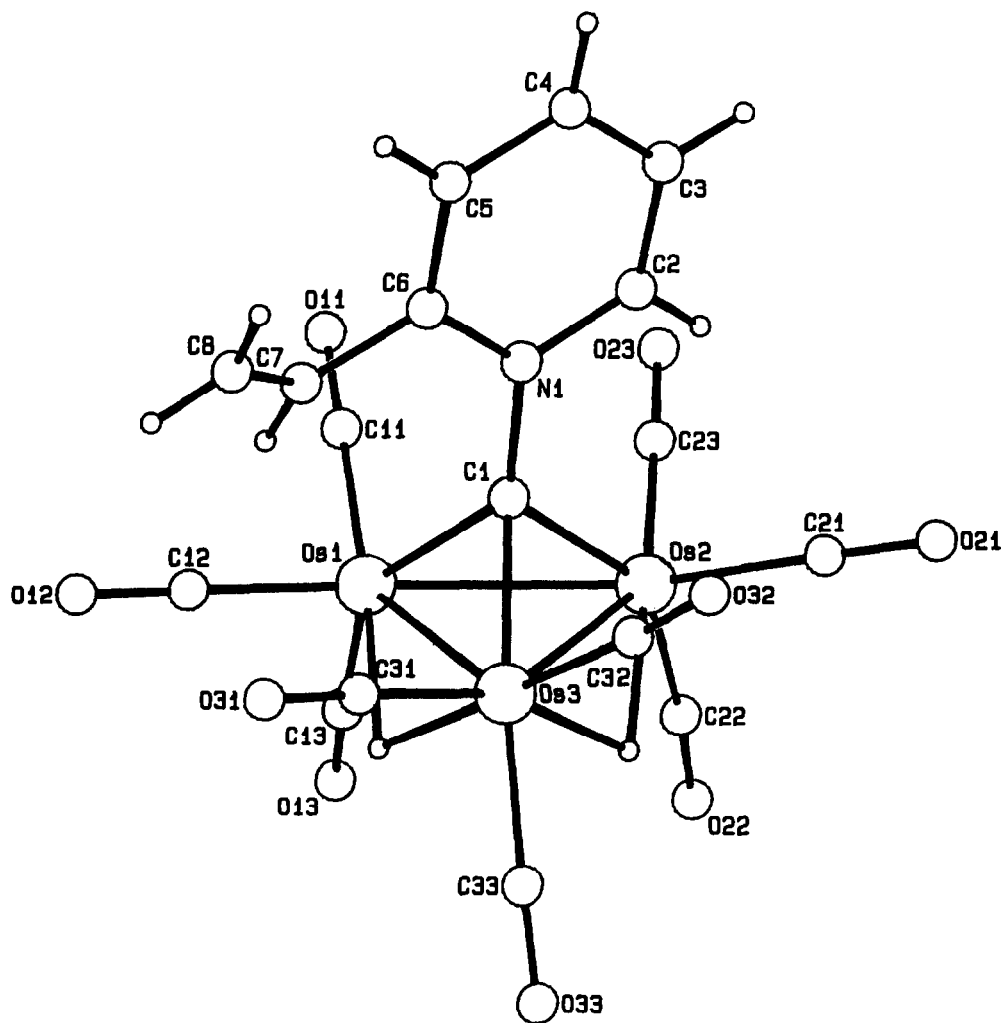


Fig. 1. The molecular structure of $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-CNC}_5\text{H}_4\text{-CH=CH}_2)]$ (1) showing the atom numbering scheme. Selected bond lengths and angles: Os(1)–Os(2), 2.7478(7); Os(1)–Os(3), 2.8622(7); Os(2)–Os(3), 2.8813(7); Os(1)–C(1), 2.12(1); Os(2)–C(1), 2.10(2); Os(3)–C(1), 2.12(1); N(1)–C(1), 1.49(2); N(1)–C(2), 1.36(2); N(1)–C(6), 1.37(2); C(7)–C(8), 1.39(2) Å. Os(2)–Os(1)–Os(3), 61.77(2); Os(1)–Os(2)–Os(3), 61.07(2); Os(1)–Os(3)–Os(2), 57.16(2); Os(1)–C(1)–N(1), 133.5(8); Os(2)–C(1)–N(1), 126.3(7); Os(3)–C(1)–N(1), 128.0(8); C(6)–C(7)–C(8), 123(2)°.

π -bonding interaction from the vinyl group to the osmium atom is observed in compound 2.

As far as the bonding is concerned, both the structural features and the spectroscopic data (IR) for these two compounds are consistent with a zwitterionic formulation.

Acknowledgments

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References and notes

- 1 B.F.G. Johnson, F.J. Lahoz, J. Lewis, N.D. Prior, P.R. Raithby and W.T. Wong, *J. Chem. Soc., Dalton Trans.*, (1992) 1701.
- 2 W.-Y. Wong and W.-T. Wong, *Acta Cryst., Sect. C*, (1994) in press.
- 3 Crystal data for 1: $\text{C}_{17}\text{H}_9\text{NO}_9\text{Os}_3$, $M = 941.86$, triclinic, Space group $P\bar{1}$ (No. 2); $a = 8.843(3)$, $b = 10.769(2)$, $c = 11.241(3)$ Å; $\alpha = 91.86(2)$, $\beta = 96.22(2)$, $\gamma = 91.62(2)^\circ$; $V = 1063.1(7)$ Å³, $Z = 2$, $D_c = 2.942$ g cm⁻³, $F(000) = 836$, Mo-K α radiation, $\lambda = 0.71073$ Å, $\mu(\text{Mo-K}\alpha) = 179.59$ cm⁻¹. Orange block, crystal dimensions:

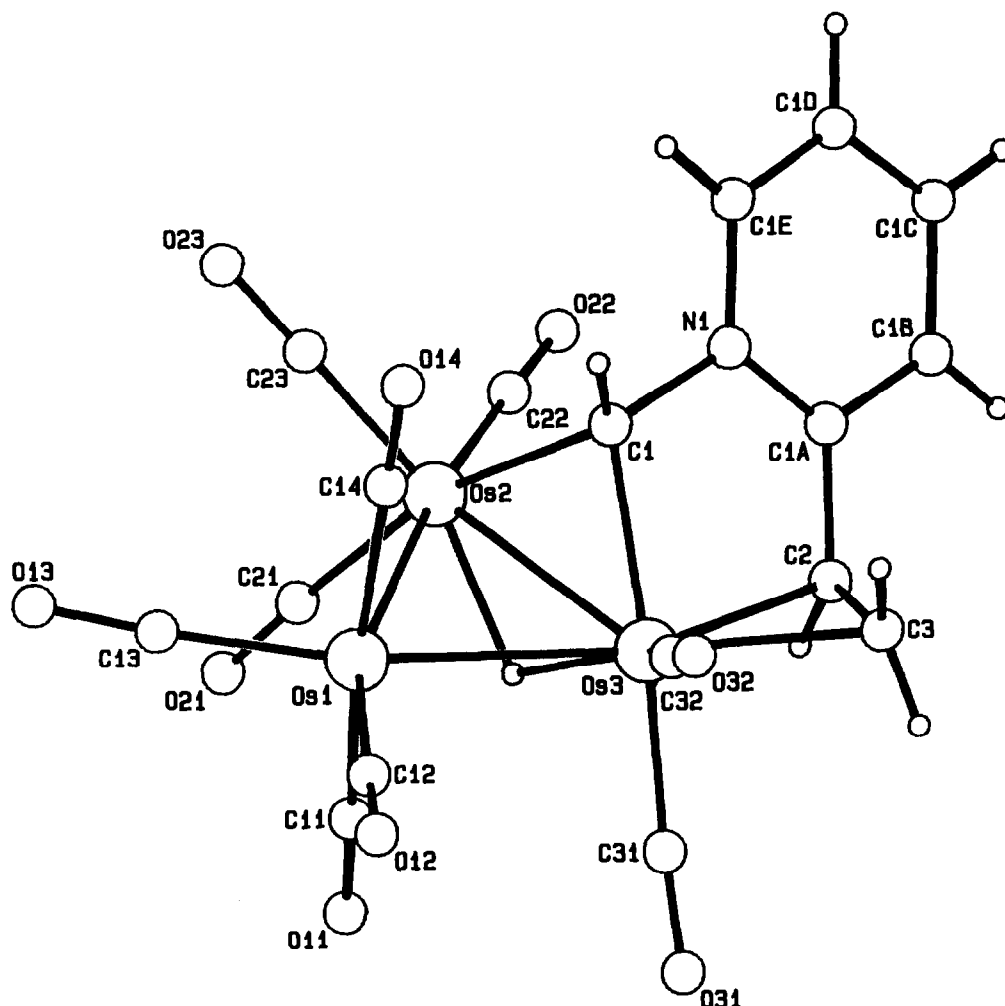


Fig. 2. The molecular structure of $[\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu\text{-C(H)NC}_5\text{H}_4\text{-}\eta^2\text{-CH=CH}_2)]$ (2) showing the atom numbering scheme. Selected bond lengths and angles: Os(1)–Os(2), 2.8617(8); Os(1)–Os(3), 2.8470(7); Os(2)–Os(3), 2.8057(7); Os(2)–C(1), 2.19(2); Os(3)–C(1), 2.12(2); Os(3)–C(2), 2.18(1); Os(3)–C(3), 2.19(1); N(1)–C(1), 1.51(2); C(2)–C(3), 1.43(2) Å. Os(2)–Os(1)–Os(3), 58.88(2); Os(1)–Os(2)–Os(3), 60.31(2); Os(1)–Os(3)–Os(2), 60.82(2); Os(2)–C(1)–Os(3), 81.1(3); Os(2)–C(1)–N(1), 113.2(8); Os(3)–C(1)–N(1), 111.4(7); Os(3)–C(2)–C(1A), 110.9(8); Os(3)–C(2)–C(3), 71.2(8); Os(3)–C(3)–C(2), 70.7(7); C(1A)–C(2)–C(3), 118.2°.

$0.22 \times 0.34 \times 0.44 \text{ mm}^3$, 3183 data measured on an Enraf–Nonius CAD4 diffractometer ($2.0 < 2\theta < 46.0^\circ$), corrected for absorption, 2398 unique observed reflections [$F > 3\sigma(F)$]. Structure solved by direct methods (MULTAN) and Fourier difference techniques, refined by full-matrix least squares analysis with 136 parameters (Os anisotropic) to $R = 0.032$, $R_w = 0.041$.

4 Crystal data for 2: $\text{C}_{17}\text{H}_9\text{NO}_9\text{Os}_3$, $M = 941.86$, monoclinic, Space group $P2_1/n$ (nonstandard setting of $P2_1/c$); $a = 12.247(2)$, $b = 9.509(2)$, $c = 18.461(2)$ Å; $\beta = 104.28(2)^\circ$; $V = 2083.5(5)$ Å³, $Z = 4$, $D_c = 3.002 \text{ g cm}^{-3}$, $F(000) = 1672$, Mo–K α radiation, $\lambda = 0.71073$ Å, $\mu(\text{Mo–K}\alpha) = 183.26 \text{ cm}^{-1}$. Yellow plate, crystal dimensions: $0.18 \times 0.32 \times 0.32 \text{ mm}^3$, 3080 data measured on an Enraf–Nonius CAD4 diffractometer ($2.0 < 2\theta < 45.0^\circ$), corrected for absorption, 2318 unique observed reflections [$F > 3\sigma(F)$]. Struc-

ture solved by direct methods (MULTAN) and Fourier difference techniques, refined by full-matrix least squares analysis with 136 parameters (Os anisotropic) to $R = 0.032$, $R_w = 0.047$. In both 1 and 2, hydrogen atoms were placed in idealised positions and were allowed to ride on the relevant carbon (C–H, 0.96 Å). The hydride atoms positions were estimated by potential energy calculations. Atomic coordinates and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

- 5 A.G. Orpen, *J. Chem. Soc., Dalton Trans.*, (1980) 2509.
- 6 A.P. Humphries and H.D. Kaesz, *Prog. Inorg. Chem.*, 2 (1979) 145.
- 7 M.R. Churchill and B.G. DeBoer, *Inorg. Chem.*, 16 (1977) 1141.
- 8 W.Y. Yeh, H.J. Kneuper and J.R. Shapley, *Polyhedron*, 7 (1988) 961.