

Coupling reaction of alkyl cyanide (RCN, R = Me or Et) with 7-azaindole on a hexaosmium carbonyl cluster core; molecular structure of $[\text{Os}_6(\text{CO})_{14}(\mu\text{-CO})(\mu\text{-H})(\mu\text{-}\eta^1:\eta^2\text{-C}_9\text{H}_8\text{N}_3)]$

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Treatment of $[\text{Os}_6(\text{CO})_{16}(\text{NCR})_2]$ (R = Me or Et) with 7-azaindole resulted in the formation of $[\text{Os}_6(\text{CO})_{14}(\mu\text{-CO})(\mu\text{-H})(\mu\text{-}\eta^1:\eta^2\text{-C}_9\text{H}_8\text{N}_3)(\text{R})]$ involving coupling of the alkyl cyanide and 7-azaindole.

The interaction of two organic fragments bound to the metal cluster core to give a larger and more complex molecular fragment is of basic scientific interest and has potential industrial applications.¹ We are currently interested in the study of transition-metal cluster assisted coupling of organic molecules and have recently observed some ruthenium clusters with a co-ordinated phenoxazinone-like ligand that arose from a 'quinone-imine or -nitrene' intermediate *via* the reductive deoxygenation of the quinone-oxime by the transition-metal carbonyl cluster.² As part of our continuing investigations, we have studied the interaction of 7-azaindole with the hexaosmium cluster $[\text{Os}_6(\text{CO})_{16}(\text{NCR})_2]$ and observed that a novel coupling between the co-ordinated acetonitrile ligand and 7-azaindole gave a metallaheterocycle involving osmium metal.

Reaction of 1 equivalent of 7-azaindole with the preformed labile bis(acetonitrile)hexaosmium carbonyl cluster $[\text{Os}_6(\text{CO})_{16}(\text{NCR})_2]$,³ in CH_2Cl_2 , gave $[\text{Os}_6(\text{CO})_{14}(\mu\text{-CO})(\mu\text{-H})(\mu\text{-}\eta^1:\eta^2\text{-C}_9\text{H}_8\text{N}_3)]$ **1**.[‡] The stoichiometry of **1** was initially established by FAB-MS and ¹H NMR spectroscopic techniques.§ Single crystals of **1** suitable for X-ray analysis¶ were obtained from slow evaporation of a toluene- CHCl_3 solution at room temperature for 2 d. A perspective drawing of cluster **1** together with some selected bond parameters is shown in Fig. 1. This analysis revealed that complex **1** contains a bicapped-tetrahedron metal core identical to the parent compound $\text{Os}_6(\text{CO})_{18}$.⁵ However, the co-ordinated 7-azaindole ligand was found to couple with a co-ordinated acetonitrile to form three fused rings involving osmium metal [Os(6)]. Such a ring system is nearly planar with a maximum deviation of 0.30 Å. The 7-azaindole also underwent orthometallation and co-ordinated to Os(5), which is a very common observation for pyridine-containing osmium

clusters. Recently we also reported the reaction of 7-azaindole with $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ to give a major product $[\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu\text{-C}_7\text{H}_5\text{N}_2)]$ containing an orthometallated ligand.⁶ All the carbonyl ligands were terminally bonded except a bridging CO across the Os(3)-Os(6) edge. This Os-Os edge is found to be significantly shorter than other Os-Os bonds in **1** which might probably be due to the 'clamping' effect of the bridging CO. The hydride and the imine hydrogen, as evident from ¹H NMR, could not be located directly by X-ray analysis. However, potential-energy calculations⁷ suggested that the hydride bridges Os(4)-Os(5). This is also consistent with the observed long Os(4)-Os(5) distance compared with other Os-Os distances in the structure.⁸ The imino hydrogen was found to undergo dissociation in the presence of a strong base such as 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) so that a cluster anion $[\text{Os}_6(\text{CO})_{14}(\mu\text{-CO})(\mu\text{-H})(\mu\text{-}\eta^1:\eta^2\text{-C}_9\text{H}_7\text{N}_3)]^-$ **2** resulted. However, the hydride ligand does not undergo dissociation in

§ Spectroscopic data: complex **1**. IR (CH_2Cl_2 , cm^{-1}) 2086m, 2055s, 2022s, 2012vs, 1956w [$\nu(\text{CO})$]. Positive-ion FAB mass spectrum: m/z 1720 (Calc. 1720). ¹H NMR (CD_2Cl_2): δ -14.33 (s, 1 H, metal hydride), 1.26 (s, 3 H, methyl), 6.75 [dd, 1 H, H¹, $J(\text{H}^{1,2})$ 7.8, $J(\text{H}^{1,3})$ 2.0], 7.26 [dd, 1 H, H⁴, $J(\text{H}^{4,3})$ 7.7, $J(\text{H}^{4,2})$ 1.6], 7.46 [ddd, 1 H, H², $J(\text{H}^{2,1})$ 7.8, $J(\text{H}^{2,3})$ 4.3, $J(\text{H}^{2,4})$ 1.6], 7.82 [ddd, 1 H, H³, $J(\text{H}^{3,4})$ 7.7, $J(\text{H}^{3,2})$ 4.3, $J(\text{H}^{3,1})$ 2.0 Hz], 8.69 (s br, 1 H, NH) (Found: C, 18.93; H, 0.54; N, 2.44. Calc. for $\text{C}_{24}\text{H}_9\text{N}_3\text{O}_{15}\text{Os}_6\cdot 0.5\text{C}_7\text{H}_8$: C, 18.68; H, 0.74; N, 2.38%).

Complex **2**. ¹H NMR (CD_2Cl_2): δ -14.58 (s, 1 H, metal hydride), 1.26 (s, 3 H, methyl), 6.75 [dd, 1 H, H¹, $J(\text{H}^{1,2})$ 7.7, $J(\text{H}^{1,3})$ 2.0], 7.30 [dd, 1 H, H⁴, $J(\text{H}^{4,3})$ 7.5, $J(\text{H}^{4,2})$ 1.8], 7.52 [ddd, 1 H, H², $J(\text{H}^{2,1})$ 7.7, $J(\text{H}^{2,3})$ 4.3, $J(\text{H}^{2,4})$ 1.8], 7.82 [ddd, 1 H, H³, $J(\text{H}^{3,4})$ 7.5, $J(\text{H}^{3,2})$ 4.3, $J(\text{H}^{3,1})$ 2.0 Hz].

Complex **3**. IR (CH_2Cl_2 , cm^{-1}) 2019s, 1992vs, 1967s [$\nu(\text{CO})$]. Positive-ion FAB mass spectrum: m/z 1749 (Calc. 1748). ¹H NMR (CD_2Cl_2): δ -14.46 (s, 1 H, metal hydride), 1.25 (s, 3 H, methyl), 6.50 [dd, 1 H, H¹, $J(\text{H}^{1,2})$ 7.8, $J(\text{H}^{1,3})$ 1.9], 7.22 (dd, 1 H, H⁴, $J(\text{H}^{4,3})$ 7.5, $J(\text{H}^{4,2})$ 1.7], 7.46 [ddd, 1 H, H², $J(\text{H}^{2,1})$ 7.8, $J(\text{H}^{2,3})$ 4.2, $J(\text{H}^{2,4})$ 1.7], 7.95 [ddd, 1 H, H³, $J(\text{H}^{3,4})$ 7.5, $J(\text{H}^{3,2})$ 4.2, $J(\text{H}^{3,1})$ 1.9 Hz], 11.27 (s br, 1 H, NH).

Complex **4**. IR (CH_2Cl_2 , cm^{-1}) 2085m, 2053s, 2022s, 2012vs, 1950w [$\nu(\text{CO})$]. Positive-ion FAB mass spectrum: m/z 1734 (Calc. 1733). ¹H NMR (CD_2Cl_2): δ -15.13 (s, 1 H, metal hydride), 1.15 (t, 3 H, J 7.3, methyl), 1.41 (q, 2 H, J 7.3, methylene), 7.32 [dd, 1 H, H¹, $J(\text{H}^{1,2})$ 7.9, $J(\text{H}^{1,3})$ 1.9], 7.48 [dd, 1 H, H⁴, $J(\text{H}^{4,3})$ 7.7, $J(\text{H}^{4,2})$ 1.8], 7.82 [ddd, 1 H, H², $J(\text{H}^{2,1})$ 7.9, $J(\text{H}^{2,3})$ 4.4, $J(\text{H}^{2,4})$ 1.8], 8.23 [ddd, 1 H, H³, $J(\text{H}^{3,4})$ 7.7, $J(\text{H}^{3,2})$ 4.4, $J(\text{H}^{3,1})$ 1.9 Hz], 8.67 (s, br, 1 H, NH) (Found: C, 18.73; H, 0.79; N, 2.42. Calc. for $\text{C}_{25}\text{H}_{11}\text{N}_3\text{O}_{15}\text{Os}_6$: C, 18.89; H, 0.83; N, 2.32%).

¶ Crystal data: $\text{C}_{24}\text{H}_9\text{N}_3\text{O}_{15}\text{Os}_6\cdot 0.5\text{C}_7\text{H}_8$ **1**, $M = 1766.62$, primitive monoclinic, space group $P2_1/n$ (no. 14, non-standard setting of $P2_1/c$), $a = 10.223(1)$, $b = 28.137(2)$, $c = 12.357(1)$ Å, $\beta = 97.70(1)^\circ$, $U = 3522.4(5)$ Å³, $Z = 4$, $D_c = 3.331$ g cm⁻³, $T = 298$ K, $F(000) = 3100$, Mo-K α radiation ($\lambda = 0.71073$ Å), $\mu(\text{Mo-K}\alpha) = 216.17$ cm⁻¹, dimensions $0.12 \times 0.12 \times 0.18$ mm, 4002 observed diffractometer data [$I > 1.0\sigma(I)$]. The structure was solved by direct methods (SIR 88)⁴ and Fourier-difference techniques, refined by full-matrix least-squares analysis on F to $R = 0.074$, $R' = 0.073$, $w = 1/\sigma^2(F_o)$. A disordered toluene solvate was found and located on a centre of inversion. Therefore, the methyl group [C(28)] on the toluene molecule was assigned an occupancy factor of 0.5. Refinement with this model led to reasonable thermal parameters for this molecule. CCDC reference number 186/997.

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[‡] Treatment of 7-azaindole (7.1 mg) with $[\text{Os}_6(\text{CO})_{16}(\text{NCR})_2]$ (100 mg, 0.06 mmol) in CH_2Cl_2 (25 cm³) under ambient conditions over a period of 24 h afforded a deep brown reaction mixture. Purification by TLC on silica Merck Kieselgel 60 GF₂₅₄ (hexane- CH_2Cl_2 , 1:3) gave the brown air-stable cluster **1** (35%) together with two uncharacterized products in low yields. Deprotonation of **1** (10 mg) with a slight excess of dbu was carried out in CH_2Cl_2 (10 cm³) at room temperature. Proton NMR monitoring indicated that the deprotonation to give **2** was complete within 10 min. The subsequent reprotonation of **2** to give **1** was achieved by the addition of excess trifluoroacetic acid (0.2 cm³). Carbonylation of **1** (20 mg) was carried out in CH_2Cl_2 (30 cm³) at room temperature for 4 h to give the light brown cluster **3**. Due to the instability of **3** in solution no accurate yield could be determined. A similar synthetic methodology to **1** was used for the preparation of **4** with EtCN instead of MeCN (yield 30%).

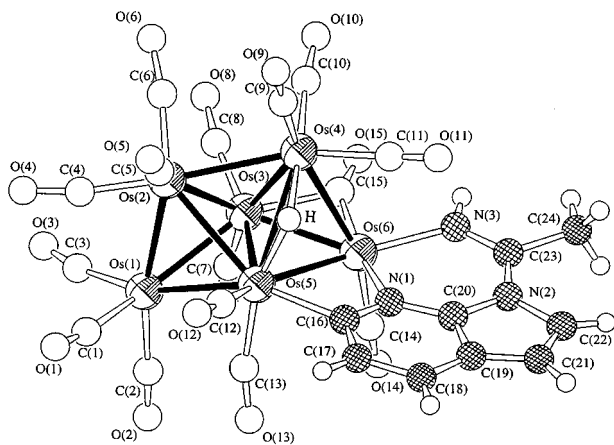


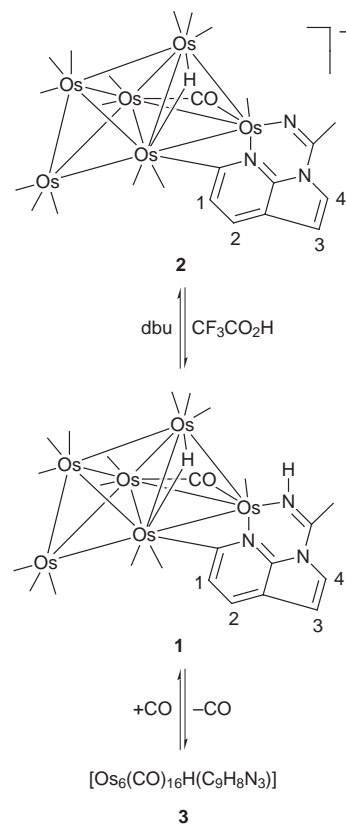
Fig. 1 Molecular structure of $[\text{Os}_6(\text{CO})_{14}(\mu\text{-CO})(\mu\text{-H})(\text{C}_9\text{H}_8\text{N}_3)]$ **1** showing the atomic numbering scheme. Selected bond lengths (Å) and angles ($^\circ$): Os(1)–Os(2) 2.764(2), Os(1)–Os(3) 2.732(2), Os(1)–Os(5) 2.877(2), Os(2)–Os(3) 2.717(1), Os(2)–Os(5) 2.889(2), Os(3)–Os(5) 2.793(2), Os(2)–Os(4) 2.824(2), Os(3)–Os(4) 2.827(2), Os(4)–Os(5) 2.903(1), Os(3)–Os(6) 2.598(2), Os(4)–Os(6) 2.927(2), Os(5)–Os(6) 2.820(1), Os(5)–C(16) 2.11(3), Os(6)–N(1) 2.08(2), Os(6)–N(3) 2.11(2), N(3)–C(23) 1.32(3), N(2)–C(23) 1.35(3), N(2)–C(20) 1.39(4), N(1)–C(20) 1.36(3); Os(6)–N(3)–C(23) 129(1), N(3)–C(23)–N(2) 124(2), C(23)–N(2)–C(20) 124(2), N(2)–C(20)–N(1) 127(2), C(20)–N(1)–Os(6) 124(1), N(1)–Os(6)–N(3) 85.4(8)

the presence of excess dbu. The reaction was reversible as **2** converted to **1** quantitatively with addition of $\text{CF}_3\text{CO}_2\text{H}$, see Scheme 1. Cluster **1** also reacted with CO at room temperature to give an unstable compound with a molecular formula of $[\text{Os}_6(\text{CO})_{16}\text{H}(\text{C}_9\text{H}_8\text{N}_3)]$ **3**. However, attempts to obtain single crystals for X-ray analysis have met with little success. Cluster **3** was unstable in solution and reverted back to **2** even when being kept in the CO atmosphere.

The coupling reaction of 7-azaindole with the co-ordinated cyanides is also applicable for ethyl cyanide. The analogous compound $[\text{Os}_6(\text{CO})_{14}(\mu\text{-CO})(\mu\text{-H})(\text{C}_{10}\text{H}_{10}\text{N}_3)]$ **4** was isolated as the major product (30%) and characterized by solution spectroscopic methods \S and is believed to have a similar structure to **1**. However, extension of this work to phenyl cyanide is hampered by the poor stability of the precursor complex $[\text{Os}_6(\text{CO})_{16}(\text{NCPH}_2)]$. Interaction of co-ordinated cyanide ligands with other organic ligands on the co-ordination sphere of the cluster core is rather rare. Previously it was believed that the cyanide ligands, in particular MeCN , were good leaving groups and serve as labile substituents for substitution chemistry of transition-metal clusters. Although recent work indicates that the co-ordinated acetonitrile is not necessarily displaceable in the higher nuclearity systems such as $[\text{Os}_6(\text{CO})_{15}\text{H}(\text{MeCN})(\text{C}_5\text{H}_5\text{N})(\text{C}_5\text{H}_4\text{N})]$, 9 $[\text{Os}_6(\text{CO})_{20}(\mu_4\text{-S})(\text{MeCN})]$ 10 and $[\text{Os}_6\text{Pt}(\text{CO})_{17}\text{H}(\mu_3\text{-NCMe})(\text{C}_8\text{H}_{12})]$. 11

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Scheme 1

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