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Coupling reaction of alkyl cyanide (RCN, R = Me or Et) with 7-azaindole on a hexaosmium carbonyl cluster core; molecular structure of $[Os_6(CO)_{14}(\mu\text{-}CO)(\mu\text{-}H)(\mu\text{-}\eta^1:\eta^2\text{-}C_9H_8N_3)]$

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Treatment of $[Os_6(CO)_{16}(NCR)_2]$ (R = Me or Et) with 7-azaindole resulted in the formation of $[Os_6(CO)_{14}(\mu\text{-}CO)(\mu\text{-}H)(\mu\text{-}\eta^1:\eta^2\text{-}C_8H_5N_3)(R)]$ 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 $[Os_6(CO)_{16}(NCMe)_2]$ 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 $[Os_6(CO)_{16}(NCMe)_2]$,[3] in CH_2Cl_2, gave $[Os_6(CO)_{14}(\mu\text{-}CO)(\mu\text{-}H)(\mu\text{-}\eta^1:\eta^2\text{-}C_9H_8N_3)]$ **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 $Os_6(CO)_{18}$.[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 $[Os_3(CO)_{10}(NCMe)_2]$ to give a major product $[Os_3(\mu\text{-}H)(CO)_9(\mu\text{-}C_7H_5N_2)]$ 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 calculations[7] 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 $[Os_6(CO)_{14}(\mu\text{-}CO)(\mu\text{-}H)(\mu\text{-}\eta^1:\eta^2\text{-}C_9H_7N_3)]^-$ **2** resulted. However, the hydride ligand does not undergo dissociation in

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[‡] Treatment of 7-azaindole (7.1 mg) with $[Os_6(CO)_{16}(NCMe)_2]$ (100 mg, 0.06 mmol) in CH_2Cl_2 (25 cm^3) under ambient conditions over a period of 24 h afforded a deep brown reaction mixture. Purification by TLC on silica Merck Kieselgel 60 GF_{254} (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 cm^3) 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 cm^3). Carbonylation of **1** (20 mg) was carried out in CH_2Cl_2 (30 cm^3) 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%).

[§] Spectroscopic data: complex **1**. IR (CH_2Cl_2, cm^{-1}) 2086m, 2055s, 2022s, 2012vs, 1956w [ν(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, H^1, $J(H^{1,2})$ 7.8, $J(H^{1,3})$ 2.0], 7.26 [dd, 1 H, H^4, $J(H^{4,3})$ 7.7, $J(H^{4,2})$ 1.6], 7.46 [ddd, 1 H, H^2, $J(H^{2,1})$ 7.8, $J(H^{2,3})$ 4.3, $J(H^{2,4})$ 1.6], 7.82 [ddd, 1 H, H^3, $J(H^{3,4})$ 7.7, $J(H^{3,2})$ 4.3, $J(H^{3,1})$ 2.0 Hz], 8.69 (s br, 1 H, NH) (Found: C, 18.93; H, 0.54; N, 2.44. Calc. for $C_{24}H_9N_3O_{15}Os_6\cdot 0.5C_7H_8$: 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, H^1, $J(H^{1,2})$ 7.7, $J(H^{1,3})$ 2.0], 7.30 [dd, 1 H, H^4, $J(H^{4,3})$ 7.5, $J(H^{4.2})$ 1.8], 7.52 [ddd, 1 H, H^2, $J(H^{2,1})$ 7.7, $J(H^{2,3})$ 4.3, $J(H^{2,4})$ 1.8], 7.82 [ddd, 1 H, H^3, $J(H^{3,4})$ 7.5, $J(H^{3,2})$ 4.3, $J(H^{3,1})$ 2.0 Hz].

Complex **3**. IR (CH_2Cl_2, cm^{-1}) 2019s, 1992vs, 1967s [ν(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, H^1, $J(H^{1,2})$ 7.8, $J(H^{1,3})$ 1.9], 7.22 (dd, 1 H, H^4, $J(H^{4,3})$ 7.5, $J(H^{4,2})$ 1.7], 7.46 [ddd, 1 H, H^2, $J(H^{2,1})$ 7.8, $J(H^{2,3})$ 4.2, $J(H^{2,4})$ 1.7], 7.95 [ddd, 1 H, H^3, $J(H^{3,4})$ 7.5, $J(H^{3,2})$ 4.2, $J(H^{3,1})$ 1.9 Hz], 11.27 (s br, 1 H, NH).

Complex **4**. IR (CH_2Cl_2, cm^{-1}) 2085m, 2053s, 2022s, 2012vs, 1950w [ν(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, H^1, $J(H^{1,2})$ 7.9, $J(H^{1,3})$ 1.9], 7.48 [dd, 1 H, H^4, $J(H^{4,3})$ 7.7, $J(H^{4,2})$ 1.8], 7.82 [ddd, 1 H, H^2, $J(H^{2,1})$ 7.9, $J(H^{2,3})$ 4.4, $J(H^{2,4})$ 1.8], 8.23 [ddd, 1 H, H^3, $J(H^{3,4})$ 7.7, $J(H^{3,2})$ 4.4, $J(H^{3,1})$ 1.9 Hz], 8.67 (s, br, 1 H, NH) (Found: C, 18.73; H, 0.79; N, 2.42. Calc. for $C_{25}H_{11}N_3O_{15}Os_6$: C, 18.89; H, 0.83; N, 2.32%).

[¶] Crystal data: $C_{24}H_9N_3O_{15}Os_6\cdot 0.5C_7H_8$ **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, $\beta = 97.70(1)°$, $U = 3522.4(5)$ Å^3, $Z = 4$, $D_c = 3.331$ g cm^{-3}, $T = 298$ K, $F(000) = 3100$, Mo-Kα radiation (λ = 0.710 73 Å), μ(Mo-Kα) = 216.17 cm^{-1}, dimensions 0.12 × 0.12 × 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.

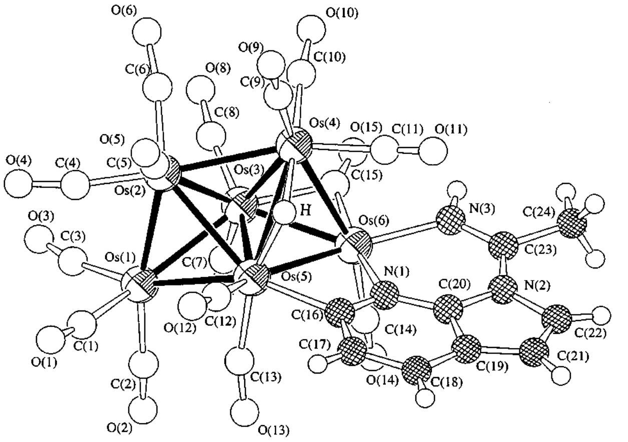

Fig. 1 Molecular structure of $[Os_6(CO)_{14}(\mu\text{-}CO)(\mu\text{-}H)(C_9H_8N_3)]$ **1** showing the atomic numbering scheme. Selected bond lengths (Å) and angles (°): Os(1)–Os(2) 2.764(2), Os(1)–Os(3) 2.732(2), Os(1)–Os(5) 2.877(2), Os(2)–Os(3) 2.717(1), Os(2)–Os(5) 2.889(2), Os(3)–Os(5) 2.793(2), 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 CF_3CO_2H, see Scheme 1. Cluster **1** also reacted with CO at room temperature to give an unstable compound with a molecular formula of $[Os_6(CO)_{16}H(C_9H_8N_3)]$ **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 $[Os_6(CO)_{14}(\mu\text{-}CO)(\mu\text{-}H)(C_{10}H_{10}N_3)]$ **4** was isolated as the major product (30%) and characterized by solution spectroscopic methods§ 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 $[Os_6(CO)_{16}(NCPh)_2]$. 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 $[Os_6(CO)_{15}H(MeCN)(C_5H_5N)(C_5H_4N)]$,[9] $[Os_6(CO)_{20}(\mu_4\text{-}S)(MeCN)]$[10] and $[Os_6Pt(CO)_{17}H(\mu_3\text{-}NCMe)(C_8H_{12})]$.[11]

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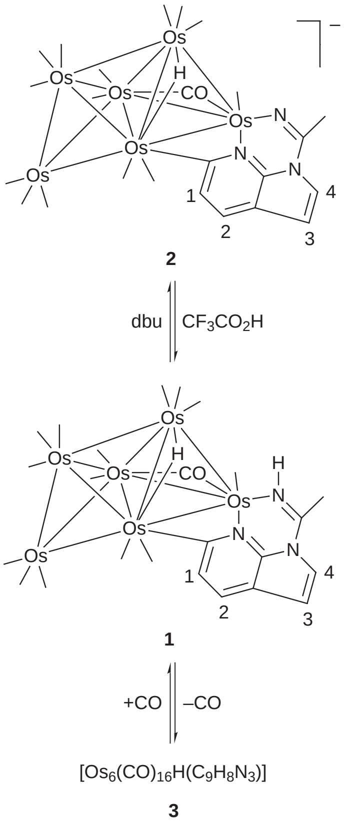

Scheme 1

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