Supplementary Information for

Normal and Abnormal NHC Coordination in $[Os_4(\mu\text{-}H)_4(CO)_{11}(IMes)]$ and Exhaustive Dehydrogenation of an IMes Methyl Group

Craig E. Cooke [a], Michael C. Jennings [b], and Roland K. Pomeroy [a] and Jason A. C. Clyburne*[c]

a Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby BC V5A 1S6, Canada

b Department of Chemistry, University of Western Ontario, 1151 Richmond St, London ON N6A 5B7 Canada

c Department of Chemistry, Saint Mary's University, Halifax NS, B3H 3C3, Canada.

General considerations: Care should be exercised when working with both osmium carbonyls due to health and exposure risks. Unless otherwise stated, manipulations of starting materials and products were carried out under a nitrogen atmosphere with the use of standard Schlenk techniques. Solvents were thoroughly dried before use.

Synthetic procedures and selected characterization data:

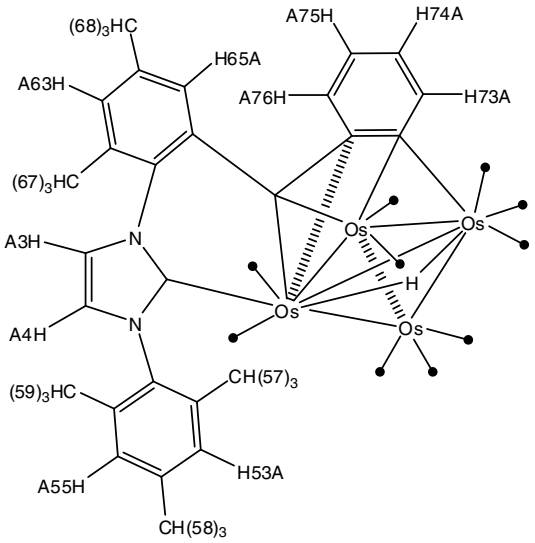
(**1**·nIMes): $[Os_4(\mu\text{-}H)_4(CO)_{11}(CO)]$ (1·CO) (110 mg, 0.1 mmol) in CH_2Cl_2 (50 mL) was stirred with two equivalents of trimethylamine *N*-oxide (15mg, 0.2mmol) in CH_2Cl_2 (20 mL) being added drop wise over 20 minutes at 0°C. Subsequently, [(IMes)AgCl]) (47.1mg, 0.1mmol) was then added. After stirring for two hours the solution had changed color from yellow to dark orange-brown. The appearance of grey AgCl(s) in the bottom of the reaction vessel was used to determine reaction completion. The solvent was removed *in vacuo* and the remaining solid dissolved in a minimum of CH_2Cl_2 and applied to a silica gel column. Elution under a 20% solution of CH_2Cl_2 to hexanes afforded a single orange-yellow band of (**1**·nIMes), (29 mg, 21%).

(**1**·nIMes): IR(in CH_2Cl_2) ν(CO): 2094 sh, 2085 m, 2064 sh, 2053 vs, 2045 s ,2023 s, 2011 sh, 1996 m,br, 1979 m, 1951 w cm^{-1}. ^1H NMR (500 MHz, 295 K, CD_2Cl_2) δ -20.14 [s,br, μ-H], 2.12 [s, 12H, *ortho*-CH_3], 2.35 [s, 6H, *para*-CH_3] , 7.05 [s, 4H, *meta*-H], 7.09 [d, 2H, *im*-H]. $^{13}C\{^1H\}$ NMR (100.61 MHz, 295 K, CD_2Cl_2) δ 19.4 [s, *o*-CH_3], 21.4 [s, *p*-CH_3], 124.9 [s, *NCC*], 130.5 [s, *Ar-C*-3,5], 135.9 [s, *Ar-C*-2,6], 137.1 [s, *Ar-C1*,], 141.0 [s, *Ar-C-4*]. MS (LSIMS) 1377.9 (P+). Anal. Calc. for $C_{32}H_{28}N_2O_{11}Os_4$ C, 27.90, H 2.05, N 2.03. Found C, 27.77, H, 2.10, N 1.93.

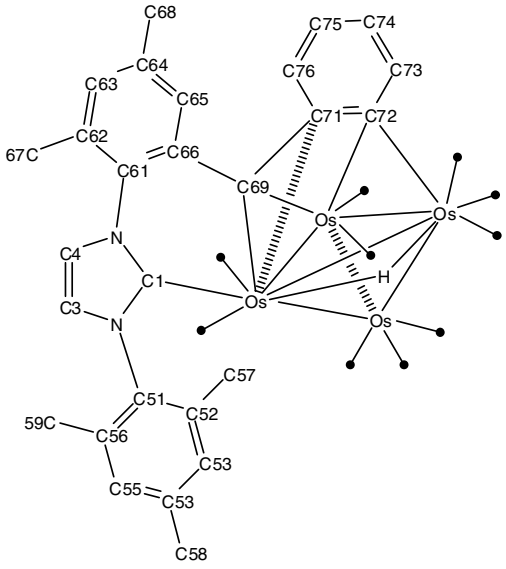
(**1**·aIMes): (**1**·nIMes) (184 mg, 0.133 mmol) was dissolved in benzene (15 mL) and heated to 200°C in a Carius tube degassed three times by freeze-pump-thaw techniques. After 72 hours the solution was cooled and solvent removed *in vacuo*. The remaining solid was dissolved in a minimum of CH_2Cl_2 and applied to a silica gel column. IR spectroscopic studies were performed on the reaction mixtures before and after column chromatography, and these studies indicated that no rearrangements occurred on the column. Compound (**1**·aIMes) was eluted in a 20% CH_2Cl_2 solution of hexanes as a yellow band (63 mg, 34%). **2** was eluted in a 20% CH_2Cl_2 solution of hexanes as a red-brown band (31 mg, 16%). IR spectroscopic evidence was found to support the existence of trace quantities of one other product tentatively assigned to an NHC-Os_6 cluster.

(**1**·aIMes): IR (in CH_2Cl_2) ν(CO): 2084 m, 2052 vs, 2038 s, 2021 s, 1995 m, 1985 m, 1977 m, 1942 br,sh,w cm^{-1}. ^1H NMR (600 MHz, 295 K, CD_2Cl_2) δ -20.50 [s,1H,], -19.85 [s,2H, μ-H], -19.85 [s,1H, μ-H], 2.07 [s, 3H, *o*-CH_3], 2.09 [s, 3H, *o*-CH_3], 2.11 [s, 3H, *o*-CH_3], 2.2 [s,br, 3H, *o*-CH_3], 2.2 [s,br, 6H, *p*-CH_3], 6.63 [s, 1H, *meta*-H], 6.68 [s, 2H, *meta*-H], 7.04 [s, 1H, im-H], 7.07 [s, 1H, im-H], 7.09 [s, 2H, im-H], 7.95 [s, 2H, C(1)-H], 7.99 [s, 1H, C(1)-H]. $^{13}C\{^1H\}$ NMR (150.92 MHz, 295 K, CD_2Cl_2) δ 17.3 [s, *o*-CH_3], 17.4 [s, *o*-CH_3], 18.3 [s, *o*-CH_3], 21.4 [s, *p*-CH_3], 21.5 [s, *p*-CH_3], 126.0 [s, *N**C**a·NHC·C*], 129.9 [s, *Ar-C*-3,5], 130.1 [s, *Ar-C*-3,5], 130.2 [s, *Ar-C*-3,5], 131.4 [s, *Ar-C*-3,5], 134.1 [s, *Ar-C*-2,6], 134.2 [s, *Ar-C*-2,6], 134.4 [s, *Ar-C*-2,6], 134.7 [s, *Ar-C*-2,6] 135.0 [s, *Ar-C1*],136.0 [s, *Ar-C1*,], 141.4 [s, *Ar-C-4*], 141.9 [s, *Ar-C-4*], 177.4 [s, NC**a·*NHC·C***] MS (LSIMS) 1377.9 (P^+). Anal. Calc. for $C_{32}H_{28}N_2O_{11}Os_4$ C, 27.90, H 2.05, N 2.03. Found C, 27.41, H, 2.04, N 2.24.

2: IR(in CH_2Cl_2) ν(CO): 2076 s, 2044 vs, 2013 s, 1996 s, 1980 m, 1969 m, 1916 br,w cm^{-1}. ^1H NMR (600 MHz, 295 K, CD_2Cl_2) δ -19.95 [s, μ-H], 1.32 [s, 3H, H57], 2.20 [s, 3H, H59], 2.30 [s, 3H, H58], 2.33 [s, 3H, H67], 2.59 [s, 3H, H68], 6.86 [m, 1H, H75A], 6.88 [s, 1H, H53A], 6.92 [s, 1H, H55A], 7.03 [s, 1H, H63A], 7.11 [s, 1H, H63A], 7.17 [d, J_{HH} = 2.3 Hz, 1H, H4A], 7.18 [m, 1H, H74A], 7.57 [d, J_{HH}= 8.7 Hz, 1H, H76A], 7.71 [d, J_{HH} = 2.3 Hz, 1H, H3A], 7.84 [d, J_{HH} = 7.8 Hz, 1H, H73A].



$^{13}C\{^{1}H\}$ NMR data and tentative assignments (150.91 MHz, 295K, CD_2Cl_2) δ 18.5 [s, C57], 19.7 [s, C59], 20.5 [s, C67], 21.0 [s, C68] , 21.3 [s, C58], 120.6 [s, C53], 123.8 [s, C4] , 123.9 [s, C3], 128.1 [s, C55], 129.3 [s, C75], 129.5 [s, C63], 130.0 [s, C76], 130.8 [s, C74], 131.1 [s, C73], 132.4 [s, C65], 134.3 [s, C52], 135.8 [s, C56], 135.9 [s, C62], 136.9 [s, C51], 137.0 [s, C61], 140.8 [s, C66], 147.0 [s, C54], 148.0 [s, C64], 155.2 [s, C69], 162.9 [s, C71], 166.6 [s, C72], 181.0 [s, C1].



MS (LSIMS) 1419.7 (P+). Anal. Calc. for $C_{37}H_{26}N_2O_{10}Os_4$ C, 31.31, H 1.85, N 1.97. Found C 31.32 , H 1.99 , N 1.72.

Solution studies: (**1**·aNHC) (45 mg, 0.033 mmol) was dissolved in benzene (20 mL) and heated to 200°C in a Carius tube degassed three times by freeze-pump-thaw techniques. After 48 hrs the reaction mixture was subjected to column chromatography and the isolated materials corresponded to **2** (23 mg, 0.016 mmol) and *trace* of (**1**·aIMes). Infrared spectroscopic evidence for the generation of a small amount of $Os_4H_4(CO)_{12}$ was also observed as indicated by diagnostic bands at 2067 and 2019 cm^{-1}. Some insoluble black material was noted at the top of the column.

Crystal data: for **(1**·nIMes**)**: $C_{32}H_{28}N_2O_{11}Os_4$, Orthorhombic, Space group Pca2(1), a = 27.9147(5) Å, b = 16.5133(3) Å, c = 15.2219(2) Å, α = 90°, β = 90°, γ = 90°, V = 7016.7(2) Å^3, Z = 8, D_c = 2.608 Mg/m^3, Absorption coefficient = 14.500 mm^{-1}, R1 = 0.0839, wR2 = 0.1011 GOF = 0.969.

Crystal data: for **(1**·aIMes**)**: $C_{32}H_{28}N_2O_{11}Os_4$, triclinic, Space group P-1, a = 14.0263(5) Å, b = 15.9043(6) Å, c = 16.2287(6) Å, α = 96.672(2)°, β = 96.046(2)°, γ = 90.049(2)°, V = 3575.4(2) Å^3, Z = 4, D_c = 2.599 Mg/m^3, Absorption coefficient = 14.299 mm^{-1}, R1 = 0.0672, wR2 = 0.1781 GOF = 1.020.

Crystal data: for **(2)**: $C_{40}H_{33}N_2O_{10}Os_4$, Triclinic, Space group P-1, a = 12.3074(4) Å, b = 12.6819(4) Å, c = 14.7598(5) Å, α = 74.792(2)°, β = 87.235(2)°, γ = 62.317(2)°, V = 1961.26(11) Å^3, Z = 2, D_c = 2.476 Mg/m^3, Absorption coefficient = 12.976 mm^{-1}, R1 = 0.0552, wR2 = 0.1448 GOF = 1.040.

Also available CIFs for compounds **(1**·nIMes**), (1**·aIMes**)** and **2**.