

Supplementary Material (ESI) for Dalton Transactions
This journal is (c) The Royal Society of Chemistry 2008

SUPPORTING INFORMATION

Abnormal Coordination of Arduengo's Carbene Upon Reaction with $M_3(CO)_12$ ($M = Ru, Os$)

Matthew R. Crittal, Charles E. Ellul, Mary F. Mahon, Olly Saker and Michael K. Whittlesey*

Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK

1. Synthetic, Spectroscopic and Analytical Data	S-2
2. Data collection and refinement details for compounds 2-Ru , 2-Os , 3-Ru and 1-Os	S-3
3. X-ray crystal structure of 1-Os	S-5

1. Synthetic, Spectroscopic and Analytical Data

2-Ru. Ru₃(CO)₁₂ (0.19 g, 0.3 mmol) and IAd (0.10 g, 0.3 mmol) were dissolved in THF (5 mL) and the immediate release of bubbles of CO was observed. After 2 hr at room temperature, the solvent was removed and the product extracted in toluene (8 x 15 mL) to give **2-Ru** as a red-orange powder. Yield 0.19 g (68 %). X-ray quality crystals were obtained by recrystallisation from THF/hexane.

2-Os. Os₃(CO)₁₂ (0.05 g, 0.05 mmol) and IAd (0.20 g, 0.06 mmol) were dissolved in THF (5 mL) in an ampoule fitted with a J. Youngs PTFE tap and the solution heated at 70 °C for 3 hr. Removal of the solvent gave a red product, which was washed with 2 x 1 mL of THF to remove any imidazolium impurities. The residue was re-suspended in 2 mL THF and re-heated at 70 °C for 30 min. Layering with hexane afforded X-ray quality crystals of the compound. Yield 0.02 g (35 %).

3-Ru. A THF solution (5 mL) of **2-Ru** (0.1 g, 0.1 mmol) was heated to 70 °C for 5 hr under a slow flow of argon to remove the liberated CO. The solvent was removed and the crude product extracted in toluene (8 x 15 mL) to afford **3-Ru**. Yield 0.065 g (69 %). X-ray quality crystals were obtained by recrystallisation from CH₂Cl₂/hexane.

1-Os. Os₃(CO)₁₂ (0.05 g, 0.05 mmol) and I^tBu (0.04 g, 0.05 mmol) were dissolved in THF (5 mL) in an ampoule fitted with a J. Youngs PTFE tap and the solution heated under vacuum at 70 °C for 5 hr. Removal of the solvent gave a red product, which was extracted with a minimal amount of hot C₆H₅F. After cooling this was filtered and the filtrate layered with hexane to yield 0.14 g of **1-Os** (25 %). ¹H NMR (THF-*d*₈, 500 MHz, 298 K): δ 8.38 (d, 1H, *J*_{HH} = 1.9 Hz, C2-*H*), 6.73 (d, 1H, *J*_{HH} = 1.9 Hz, C5-*H*), 1.89 (s, 9H, ^tBu), 1.56 (s, 9H, ^tBu). ¹³C{¹H} (THF-*d*₈, 125 MHz, 298 K; carbonyl resonances were not assigned): δ 136.5 (s, Ru-C4), 132.2 (s, C2), 113.5 (s, C5), 61.0 (s, N-C), 58.2 (s, N-C), 30.5 (s, ^tBu), 30.9 (s, ^tBu). IR ν/cm⁻¹ (nujol): 2093 (CO), 2038 (CO), 2015

(CO), 2002 (CO), 1991 (CO), 1956 (CO), 1932 (CO), 1923 (CO). Anal. calcd for C₂₂H₂₀N₂O₁₁Os₃, %: C 24.95, H 1.90, N 2.65. Found, %: C 25.21, H 1.88, N 2.65.

2. Data collection and refinement details for compounds 2-Ru, 2-Os, 3-Ru and 1-Os.

Compound	2-Ru	2-Os	3-Ru	1-Os
Empirical formula	C ₃₈ H ₄₀ N ₂ O ₁₂ Ru ₃	C ₃₄ H ₃₂ N ₂ O ₁₁ Os ₃	C ₃₃ H ₃₄ Cl ₂ N ₂ O ₉ Ru ₃	C ₂₂ H ₂₀ N ₂ O ₁₁ Os ₃
Formula weight	1019.93	1215.22	976.73	1059.00
T / K	150(2) K	150(2) K	150(2) K	150(2) K
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> / Å	14.7010(1)	11.8360(2)	11.9540(1)	12.9270(1)
<i>b</i> / Å	18.5170(2)	12.6320(2)	22.9860(2)	13.3980(2)
<i>c</i> / Å	15.11500(1)	22.3790(4)	13.3710(1)	16.7890(2)
α / °	90	90	90	90
β / °	105.924(1)	90	107.636(1)	107.085(1)
γ / °	90	90	90	90
<i>U</i> / Å ³	3956.69(6)	3345.94(10)	3501.33(5)	2779.47(6)
<i>Z</i>	4	4	4	4
<i>D</i> _c / gcm ⁻³	1.712	2.412	1.853	2.531
μ / mm ⁻¹	1.194	11.430	1.486	13.738
<i>F</i> (000)	2040	2264	1936	1928
Crystal size / mm	0.13 x 0.13 x 0.12	0.07 x 0.05 x 0.05	0.25 x 0.25 x 0.15	0.30 x 0.30 x 0.22
Theta max., min. for data collection / °	2.99, 27.48	3.70, 27.50	3.55, 30.04	3.73, 27.50
Index ranges	-19<= <i>h</i> <=19; -24<= <i>k</i> <=24; -19<= <i>l</i> <=19	-15<= <i>h</i> <=15; -16<= <i>k</i> <=16; -28<= <i>l</i> <=29	-16<= <i>h</i> <=16; -32<= <i>k</i> <=32; -18<= <i>l</i> <=18	-16<= <i>h</i> <=16; -17<= <i>k</i> <=17; -21<= <i>l</i> <=21
Reflections collected	79718	7652	73592	43466
Independent reflections, <i>R</i> (int)	9050, 0.0440	7652, 0.0000	10224, 0.0490	6343, 0.0758
Reflections [<i>I</i> >2 σ (<i>I</i>)]	7727	6440	8575	6000
Data Completeness	0.998	0.956	0.998	0.994
Data / restraints / parameters	9050 / 0 / 496	7652 / 0 / 452	10224 / 1 / 446	6343 / 0 / 349
Goodness-of-fit (<i>F</i> ²)	1.078	1.032	1.047	1.213
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> >2 σ (<i>I</i>)]	0.0290, 0.0650	0.0454, 0.1015	0.0309, 0.0675	0.0340, 0.0859
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0386, 0.0694	0.0620, 0.1090	0.0424, 0.0728	0.0364, 0.0876
Max, min. residual density / eÅ ⁻³	0.899, -0.782	2.266, -1.784	1.127, -1.053	2.645, -2.509
Flack parameter	-	0.49(2)	-	-

Single crystals of compounds 2-Ru, and 2-Os, 3-Ru and 1-Os were analysed using a Nonius

Kappa CCD diffractometer and Mo(K α) radiation (λ = 0.71073 Å. The structures were solved

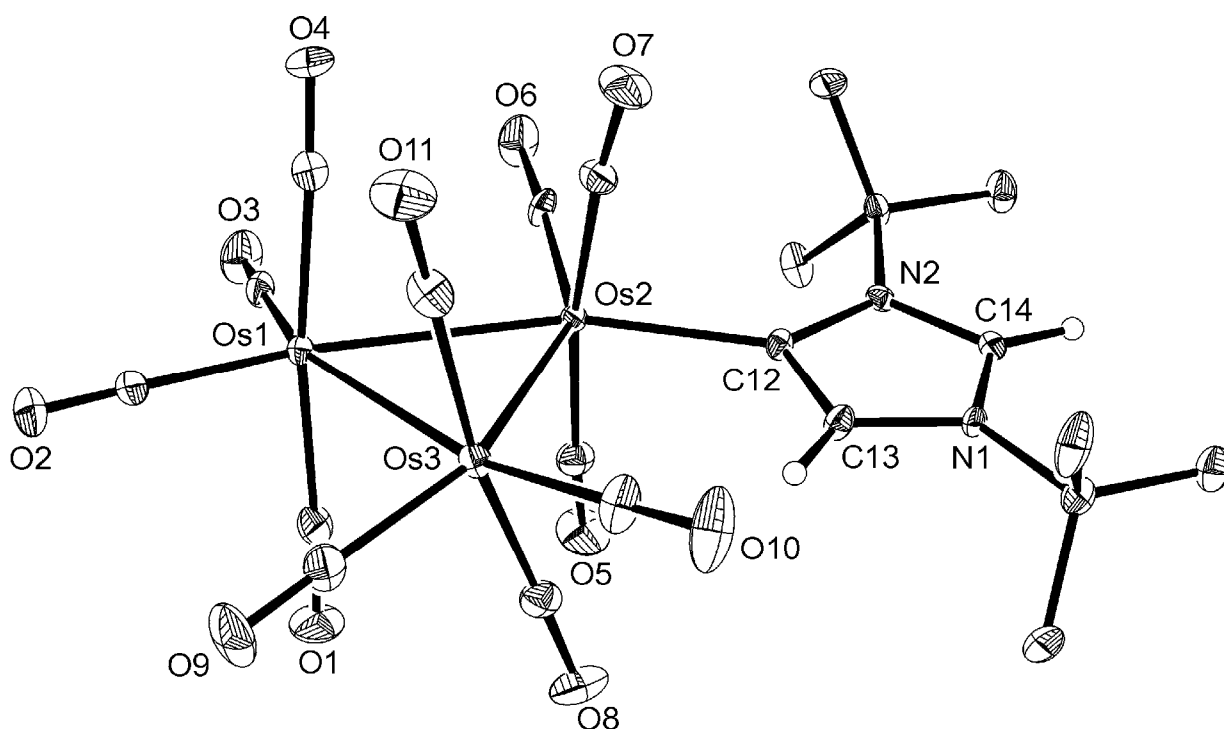
using SHELXS-97¹ and refined using full-matrix least squares in SHELXL-97.¹ Convergence was uneventful, with the exception of the following noteworthy points.

The asymmetric unit in **2-Ru**, was seen to contain one molecule of THF in addition to one molecule of the cluster. **2-Os** was something of a puzzle to unravel. Due to twinning (50%), it took extensive analysis to establish whether or not this was a monoclinic crystal or an orthorhombic one. The data set suggested that there was a glide plane absence, which initially directed the crystallographer towards $P112_1/b$ and $Pm2_1b$. However, while the gross structure was identifiable in these space groups there was ample evidence to suggest that incorrect assignment had been made. Subsequent trials with $P112_1$ and $P11b$ proved similarly unsatisfactory. Ultimately, solution in $P1$ followed by analysis of the actual lattice point symmetry resulted in assignment of the space group as presented, with an account taken for the twinning [about the (0 0 1) vector] present. Thereafter, refinement proceeded without issue, the weighting scheme stabilised, and the residual peaks present in the electron density map were seen to be at chemically insignificant distances from the Os₃ core.

In **3-Ru**, the asymmetric unit was seen to contain one molecule of dichloromethane in addition to one molecule of the cluster. Moreover, H1 was located and refined subject to being equidistant from Ru1 and Ru2.

Crystallographic data for compounds **2-Ru**, **2-Os**, **3-Ru** and **1-Os** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 687171-687174. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax(+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk].

3. X-ray crystal structure of 1-Os



Molecular structure of **1-Os**. All hydrogen atoms except those on the imidazole ring have been removed for clarity. Ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (°): Os(2)-C(12) 2.161(6), Os(1)-Os(2) 2.8658(3), Os(1)-Os(3) 2.8773(3), Os(2)-Os(3) 2.9054(3), Os(1)-Os(2)-C(12) 161.53(16), C(6)-Os(2)-C(12) 108.0(3).

1 G. M. Sheldrick, *Acta. Cryst.*, 1990, **467-473**, A46. G. M. Sheldrick, *SHELXL-97, a computer program for crystal structure refinement*, University of Göttingen, 1997.