ChemComm

Fixation and spontaneous dehydrogenation of methanol on a triruthenium–iridium framework: synthesis and structure of the cluster anion $[HRu_3Ir(CO)_{12}(OMe)]^-$

Susanne Haak,† Antonia Neels, Helen Stœckli-Evans, Georg Süss-Fink* and Christophe M. Thomas

Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, CH-2000 Neuchâtel, Switzerland.
E-Mail: GEORG.SUESS-FINK@ICH.UNINE.CH

Received (in Basel, Switzerland) 7th July 1999, Accepted 19th August 1999

The anionic mixed-metal cluster $[Ru_3Ir(CO)_{13}]^-$ 1, found to be catalytically active in the carbonylation of methanol, reacts with methanol at 70 °C to give, with O–H activation of the substrate, the cluster anion $[HRu_3Ir(CO)_{12}(OMe)]^-$ 2, which upon prolonged reaction loses formaldehyde to give the cluster anion $[H_2Ru_3Ir(CO)_{12}]^-$ 3; both anions 2 and 3 crystallise together as the double-salt $[N(PPh_3)_2]_2[HRu_3Ir(CO)_{12}(OMe)][H_2Ru_3Ir(CO)_{12}]$ the single-crystal X-ray structure analysis of which reveals a butterfly Ru_3Ir skeleton for 2 and a tetrahedral Ru_3Ir skeleton for 3.

Mixed-metal clusters have received steadily increasing attention over the last three decades owing to their inherent catalytic potential.[1] The presence of different metals in the same complex may have synergistic effects in the catalytic activity.[2] Recently we reported a series of Ru_3Ir and Os_3Ir mixed-metal clusters which show reasonable catalytic activity in the carbonylation of methanol to give acetic acid.[3,4] The cluster anions $[Ru_3Ir(CO)_{13}]^-$ **1** and $[Os_3Ir(CO)_{13}]^-$ **4**, used as catalyst precursors in this process, are however unstable under the reaction conditions, which has been confirmed by the isolation of the fragmentation products $Ir_4(CO)_{12}$ and $[N(PPh_3)_2][M(CO)_3I_3]$ (M = Ru, Os).[4] In this context we were interested in the behaviour of these anionic clusters towards reagents participating in the catalytic process, especially in the reaction with methanol.

The anion $[Ru_3Ir(CO)_{13}]^-$ **1** (as its $[N(PPh_3)_2]^+$ salt) reacts with methanol at 70 °C within 2 h to give the anionic cluster $[HRu_3Ir(CO)_{12}(OMe)]^-$ **2** [eqn. (1)], as indicated by a colour change of the solution from red to orange. The formation of **2** involves O–H activation of the methanol molecule, which is split into μ-H and μ-OMe ligands, replacing a carbonyl group of the starting compound. Anion **2** can be isolated as the $[N(PPh_3)_2]^+$ salt by extraction with diethyl ether after evaporation of the reaction solution to dryness, washing of the residue with hexane–dichloromethane (5 : 1) and recrystallisation from ethanol–pentane (1 : 3) at −18 °C.‡

$$\underset{\mathbf{1}}{[Ru_3Ir(CO)_{13}]^-} + MeOH \longrightarrow \underset{\mathbf{2}}{[HRu_3Ir(CO)_{12}(OMe)]^-} + CO \qquad (1)$$

Upon prolonged reaction (48 h) in methanol, especially at higher temperature (90 °C), anion **2** is transformed into the anion $[H_2Ru_3Ir(CO)_{12}]^-$ **3** with liberation of formaldehyde [eqn. (2)]. The formation of formaldehyde is evidenced by the ^1H NMR spectrum of the reaction mixture, which shows the signal for HCHO at δ 9.75 as well as a signal at δ 5.31 attributed to the formaldehyde trimer trioxane (by comparison with an authentic sample).

$$\underset{\mathbf{2}}{[HRu_3Ir(CO)_{12}(OMe)]^-} \longrightarrow \underset{\mathbf{3}}{[H_2Ru_3Ir(CO)_{12}]^-} + HCHO \qquad (2)$$

If the thermal reaction of **1** with methanol at 90 °C is stopped half-way (after 12 h), both anions **2** and **3** are present in the solution, and the double-salt $[N(PPh_3)_2]_2[HRu_3Ir(CO)_{12}(OMe)][H_2Ru_3Ir(CO)_{12}]$ can be isolated by crystallisation of the reaction residues from a 4 : 1 mixture of diethyl ether and hexane.

A suitable crystal§ of this double-salt revealed the molecular structure of both anions **2** and **3** (Fig. 1 and 2), disordered over the same position. Three of the four metal positions are occupied by metal atoms of both anions **2** and **3**, whereas one ruthenium atom splits into Ru(1) for anion **2** and Ru(1a) for anion **3**, the refinement of the occupancy factors giving a 1 : 1 ratio. In contrast to anion **2**, anion **3** is already known,[3] its structure in the double-salt being very similar to that we found in the salt $[N(PPh_3)_2][H_2Ru_3Ir(CO)_{12}]$.[3]

In anion **2**, the dihedral angle Ru(1)–Ir(1)–Ru(3)–Ru(2), that is to say the spreading of the wing tips is relatively small (82.9°) compared to those in other chalcogen- or halogen-bridged clusters, such as $HRu_3Co(CO)_{12}(\mu\text{-}SMe_2)$ (96.1°)[5] or $HRu_3Ir(CO)_{12}(\mu\text{-}Cl)$ (89.3°).[6] A similar dihedral angle as in **2** has been observed in the hydroxy-bridged osmium cluster cation $[H_4Os_4(CO)_{12}(\mu\text{-}OH)]^+$ (82.3°).[7] As a result of the small dihedral angle, the distance between the wing tip metal atoms Ru(1) and Ru(2) is only 3.3536(2) Å. The hydride-bridged edge Ru(1)–Ru(3), at 3.095(5) Å, is significantly longer than all the other metal–metal bonds. The wing tips are bridged asymmetrically by the methoxy group, the Ru–O bond distances being 2.02(2) and 2.16 (2) Å, respectively. This is well in line with the bond lengths found in other methoxy-bridged clusters, such as $HOs_3Pt_2(CO)_{10}(\mu_5\text{-}C)(\mu\text{-}OMe)(PCy_3)_2$[8] or $Os_3(CO)_{10}(\mu$-

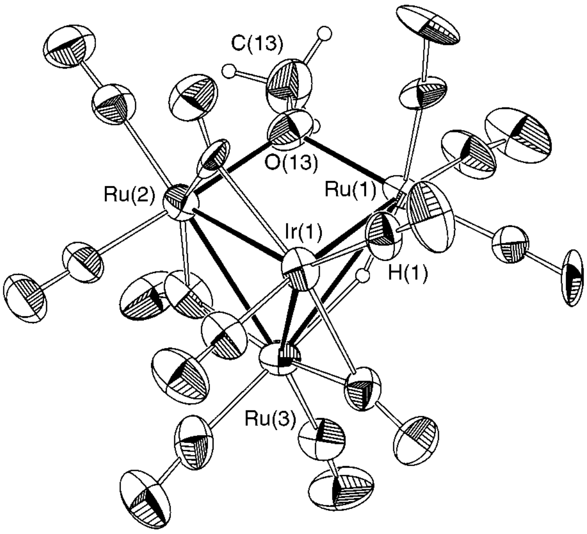


Fig. 1 Molecular structure of $[HRu_3Ir(CO)_{12}(OMe)]^-$ **2** showing the atom numbering scheme. Selected bond distances (Å) and angles (°): Ir(1)–Ru(1) 2.854(2), Ir(1)–Ru(2) 2.758(1), Ir(1)–Ru(3) 2.737(1), Ru(1)–Ru(3) 3.095(5), Ru(2)–Ru(3) 2.797(1), Ru(1)–H(1) 1.47(1), Ru(3)–H(1) 1.77(1), Ru(1)–O(13) 2.02(2), Ru(2)–O(13) 2.16(2), O(13)–C(13) 1.39(3), Ru(1)–O(13)–C(13) 119.3(16), Ru(2)–O(13)–C(13) 125.7(16).

---

† Present address: Department of Chemistry, University of Sheffield, Sheffield, UK S3 7HF.

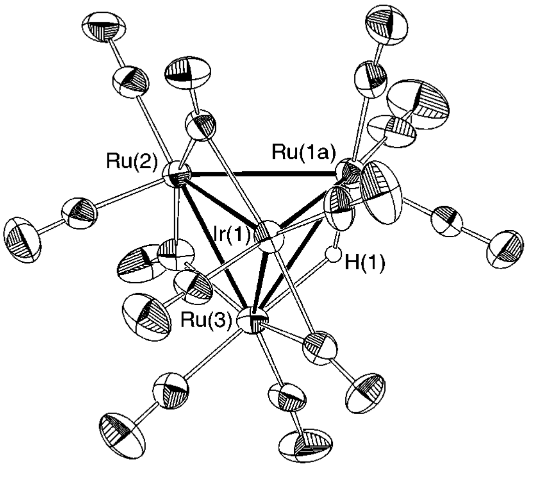
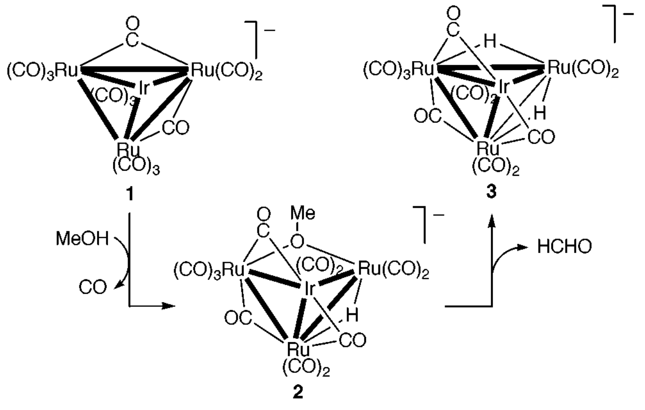


Fig. 2 Molecular structure of $[H_2Ru_3Ir(CO)_{12}]^-$ **3** showing the atom numbering scheme. Selected bond distances (Å): Ir(1)–Ru(1A) 2.689(6), Ru(1A)–Ru(2) 2.878(4), Ru(1A)–Ru(3) 2.866(6), Ru(3)–H(1) 1.77(1), Ru(1A)–H(1) 1.37(1). The second hydride ligand spanning Ru(1A)–Ru(2), only having an occupancy factor of 50%, could not be located in the double-salt, but was found in $[N(PPh_3)_2][H_2Ru_3Ir(CO)_{12}]$.[3]



Scheme 1

$OMe)_2$.[9] The methyl group sticks out of the Ru(1)–Ru(2)–O(13) plane with an angle of 13.7°, in accordance with observations for $Os_3(CO)_{10}(\mu\text{-}OMe)_2$.[9] Anion **2** is consistent with the effective atomic number rule which requires an electron count of 62 valence electrons for butterfly clusters.

The reaction sequence involving the cluster anions **1**, **2** and **3** and the oxidation of methanol to formaldehyde is very interesting (Scheme 1). Anion **1** contains a closed tetrahedral Ru_3Ir metal framework, which is opened by the reaction with methanol to give anion **2** containing a butterfly Ru_3Ir skeleton, the wing tips of which are bridged by the methoxy ligand. The elimination of formaldehyde in going from **2** to **3** implies the reclosing of the butterfly Ru_3Ir skeleton to a closed metal tetrahedron.

We are grateful to the BASF AG (Germany) for financial support of this work. We also thank the Johnson Matthey Technology Centre (United Kingdom) for a generous loan of ruthenium trichloride hydrate.

Notes and references

‡ *Analytical and spectroscopic data*: for $[N(PPh_3)_2][HRu_3Ir(CO)_{12}(OMe)]$. Analysis. Found: C, 41.97; H, 2.65; N, 1.00. Calc. for $C_{49}H_{34}IrNO_{13}P_3Ru_3$: C, 41.97; H, 2.44; N, 1.00%. IR(thf): 2071vw, 2035w, 2016s, 2006s, 1968vs, 1817m, 1805m cm^{-1}. ^1H NMR (200 MHz, 294 K, $CDCl_3$): δ −14.28 (s, 1H), 2.94 (s, 3H), 7.39–7.70 (m, 30H).

For $[N(PPh_3)_2][H_2Ru_3Ir(CO)_{12}]$. Analysis. Found: C, 41.93; H, 2.17; N, 1.08. Calc. for $C_{48}H_{32}IrNO_{12}Ru_3$: C, 42.02; H, 2.35; N, 1.02%. IR(thf): 2074w, 2038s, 2005vs, 1968m, 1952m, 1819w, 1805w cm^{-1}. ^1H NMR (200 MHz, 294 K, $CDCl_3$): δ −20.64 (s, 2H), 7.40–7.70 (m, 30H).

§ *Crystallographic data* for $[N(PPh_3)_2]_2[HRu_3Ir(CO)_{12}(OMe)][H_2Ru_3Ir(CO)_{12}]$, $C_{117}H_{66}N_2Ir_2O_{25}P_4Ru_6$, $M = 1387.18$, monoclinic, space group $P2_1/c$, $a = 14.966(1)$, $b = 19.743(1)$, $c = 17.07781)$ Å, $\beta = 98.541(10)°$, $V = 4989.8(7)$ Å^3, $Z = 2$, $D_c = 1.846$ g cm^{-3}, μ(Mo-Kα) = 3.675 mm^{-1}, 38776 reflections measured ($2\theta_{max} = 52.08°$), 5302 observed data $[I > 2\sigma(I)]$ used in the refinement, $R1 = 0.0588$, $wR2 = 0.1501$ ($R1 = 0.1042$, $wR2 = 0.1674$ for all data). Intensity data were collected at 293(2) K on a Stoe Imaging Plate Diffractometer system (IPDS) equipped with a one-circle goniometer using Mo-Kα graphite-monochromated radiation ($\lambda = 0.71073$ Å). 200 exposures (3 min per exposure) were obtained at an image plate distance of 70 mm with $0 < \varphi < 200°$ with the crystal oscillating through 1° in φ. The structure was solved by direct methods (SHELXS-97[10]) and refined using weighted full-matrix least squares on F^2 (SHELXL-97[11]). A high disorder was found in the double-salt resulting in refined occupancies of 0.5 for Ru(1), Ru(1a) and the corresponding CO ligands. The methoxy group which is coordinated to Ru(1) and Ru(2) also has an occupancy of 0.5. Despite an empirical absorption correction being applied using DIFABS[12] ($T_{min} = 0.168$, $T_{max} = 0.640$), a large peak of electron density near one of the ruthenium atoms remained, which may be due to the disorder.

CCDC 182/1387. See http://www.rsc.org/suppdata/cc/1999/1959/ for crystallographic files in .cif format.

1 P. Braunstein and J. Rose, in *Comprehensive Organometallic Chemistry 2*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Elsevier, Oxford, 1995, vol. 10, p. 351.
2 E. Rosenberg and R. M. Laine, in *Catalysis by Di- and Polynuclear Metal Complexes*, ed. R. D. Adams and F. A. Cotton, Wiley–VCH, New York, 1998, p. 1; G. Süss-Fink and M. Jahncke, in *Catalysis by Di- and Polynuclear Metal Complexes*, ed. R. D. Adams and F. A. Cotton, Wiley–VCH, New York, 1998, p. 167.
3 G. Süss-Fink, S. Haak, V. Ferrand and H. Stœckli-Evans, *J. Chem. Soc., Dalton Trans.*, 1997, 3861.
4 G. Süss-Fink, S. Haak, V. Ferrand and H. Stœckli-Evans, *J. Mol. Catal. A*, 1999, **143**, 163.
5 S. Rossi, J. Pursianen and T. A. Pakkanen, *Organometallics*, 1991, **10**, 1390.
6 A. U. Härkönen, M. Ahlgrèn, T. A. Pakkanen and J. Pursianen, *J. Organomet. Chem.*, 1996, **519**, 205.
7 B. F. G. Johnson, J. Lewis, P. R. Raithby and C. Zuccaro, *J. Chem. Soc., Dalton Trans.*, 1980, 716.
8 L. J. Farrugia, A. D. Miles and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1985, 2437.
9 V. F. Allen, R. Mason and P. B. Hitchcock, *J. Organomet. Chem.*, 1977, **140**, 297.
10 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
11 G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.
12 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1990, **46**, 158.

Communication 9/05487A