

High yield synthesis and crystal structures of the Ru₆–Sn cluster compounds [Ru₆C(CO)₁₆SnCl₂] and [Ru₆C(CO)₁₆SnCl₃][–]

Sophie Hermans and Brian F. G. Johnson*

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW.
E-mail: bfgj1@cam.ac.uk

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Addition of two molar equivalents of SnCl₄ to [Ru₆C(CO)₁₆]^{2–} yields first the new [Ru₆C(CO)₁₆SnCl₃][–] cluster anion and then [Ru₆C(CO)₁₆SnCl₂], the latter being also the single product of the direct addition of SnCl₂ to [Ru₆C(CO)₁₇].

We are currently investigating the preparation and catalytic activity of bimetallic nanoparticles derived from fully characterised bimetallic cluster compounds.^{1–3} Recent results have indicated that, once formed within the cavities of the mesoporous solid MCM-41, such nanoparticles exhibit a surprising stability and resist sintering even under moderately vigorous conditions. To this end, we have established a need for nanoparticles containing Ru–Sn cores. This association of metals is known to be highly versatile, and is used in both selective oxidation and hydrogenation catalysis.⁴ However, few Ru–Sn mixed-metal clusters have been reported.^{5–9} In this paper we report the synthesis of the new bimetallic clusters [Ru₆C(CO)₁₆SnCl₂] **2** and [Ru₆C(CO)₁₆SnCl₃][–] **4**. We regard these new cluster species as derivatives of Sn(IV) containing formally the bidentate ligand [Ru₆C(CO)₁₆]^{2–}.

The reaction sequence for the preparation of the compound [Ru₆C(CO)₁₆SnCl₂] **2** and the anion [Ru₆C(CO)₁₆SnCl₃][–] **4** is outlined in Scheme 1. Direct reaction of [Ru₆C(CO)₁₇] **1** with stannous chloride in dichloromethane is slow but over a period of several days under reflux, product **2** may be obtained in good yield (91%). The mechanism by which this reaction occurs is uncertain but would appear to take place first by simple carbon monoxide extrusion followed then by the addition of SnCl₂. However, the formal oxidation state of the Sn in **2** is (IV)[†] indicating that a redox process of the type [Ru₆C(CO)₁₆] to [Ru₆C(CO)₁₆]^{2–} occurs at some stage during the reaction sequence. In this sense, the reaction might be described as an oxidative-addition to Sn(II), leading to reduction of the cluster fragment.

In agreement, reactions of the dianionic cluster [Ru₆C(CO)₁₆]^{2–} with stannic chloride in dichloromethane produce the same Sn(IV) cluster **2** and in addition the anion [Ru₆C(CO)₁₆SnCl₃][–] **4** (as its PPN⁺ salt). Anion **4** is obtained

in 67% yield when equimolar amounts of [Ru₆C(CO)₁₆]^{2–} **3** and SnCl₄ are reacted. Treatment of **4** with further stannic chloride (1 mole) results in Cl[–] ion abstraction and the formation of **2**. The other product of this reaction is the Sn(IV) anion [SnCl₅][–]. This reaction is easily reversed, and addition of Cl[–] {as [PPN]Cl} to **2** results in the formation of **4**. The ease with which cluster **2** accepts the additional Cl[–] to generate a coordinated SnCl₃[–] group is of interest and in line with the established chemistry of SnCl₄. This emphasises the view of compound **2** as an adduct of the type XS₃Cl₂, where X = the bidentate dianionic ligand [Ru₆C(CO)₁₆]^{2–}.

Clusters **2** and **4** have been fully characterised by the usual spectroscopic and analytical techniques, and their molecular structure established by single crystal X-ray diffraction.¹⁰

The mass spectrum of **4**, obtained by ESI-MS run in negative mode, consists of a peak at *m/z* 1289, corresponding to the formulation [Ru₆C(CO)₁₆SnCl₃]. The IR spectra of **4** in the ν_{CO} stretching region consists of peaks at 2086, 2056, 2035, 2026, 1987 and 1973 cm^{–1} corresponding to terminal carbonyls, and a broad peak at 1825 cm^{–1} corresponding to bridging CO.

The molecular structure of the anion [Ru₆C(CO)₁₆SnCl₃][–] **4** is shown in Fig. 1, together with selected bond lengths and angles. It consists of the intact core of the Ru₆C(CO)₁₆ cluster, with one Ru–Ru edge bridged by a SnCl₃ fragment. It is

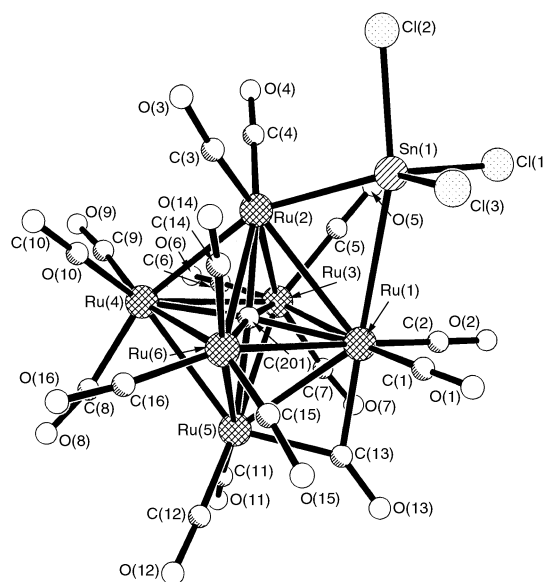
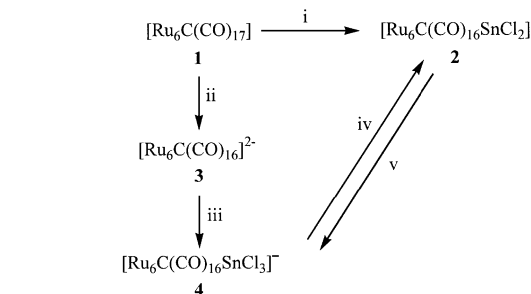


Fig. 1 Molecular structure of [Ru₆C(CO)₁₆SnCl₃][–] **4** with atom numbering scheme. Selected bond lengths (Å) and angles (°): Molecule 1: Ru(1)–Sn(1) 3.140(2), Ru(2)–Sn(1) 2.581(3), Sn(1)–Cl(1) 2.391(6), Sn(1)–Cl(2) 2.459(5), Sn(1)–Cl(3) 2.406(5), Ru(1)–Ru(2) 3.039(3), Ru–Ru (mean) 2.89(2), C–O (mean) 1.177(8), Ru(1)–Sn(1)–Ru(2) 63.28(6), Cl(1)–Sn(1)–Cl(2) 164.13(13), Cl(2)–Sn(1)–Cl(3) 93.70(19), Cl(1)–Sn(1)–Cl(3) 101.1(2). Molecule 2: Ru(7)–Sn(2) 2.583(3), Ru(8)–Sn(2) 3.102(2), Sn(2)–Cl(5) 2.478(6), Sn(2)–Cl(6) 2.371(6), Sn(2)–Cl(4) 2.386(5), Ru(7)–Ru(8) 3.043(3), Ru–Ru (mean) 2.90(3), C–O (mean) 1.17(1), Ru(7)–Sn(2)–Ru(8) 63.97(6), Cl(4)–Sn(2)–Cl(6) 101.6(2), Cl(6)–Sn(2)–Cl(5) 93.1(3), Cl(5)–Sn(2)–Cl(4) 93.8(2).



Scheme 1 Synthesis of the cluster species [Ru₆C(CO)₁₆SnCl₂] and [Ru₆C(CO)₁₆SnCl₃][–] **3**. Reagents and conditions: i, reaction with SnCl₂ in dichloromethane, reflux, 4 days; ii, reaction with KOH–MeOH; iii, reaction with SnCl₄ in dichloromethane at room temperature; iv, reaction with SnCl₄ in dichloromethane under reflux; v, reaction with [PPN]Cl in dichloromethane at room temperature.

monoanionic and the asymmetric unit of the structure contains two independent anions and two PPN⁺ cations. Fifteen carbonyl ligands are terminally bound to the ruthenium atoms, and one is bridging a Ru–Ru bond.

The geometry of the Ru₆C octahedron has remained almost unchanged, with the mean Ru–Ru bond distance of 2.89(2) Å in molecule 1 and 2.90(3) Å in molecule 2 identical to that of 2.90(2) Å found in [Ru₆C(CO)₁₇].¹¹ The Ru–Ru bond spanned by the tin atom is the longest (Ru(1)–Ru(2) 3.039(3) Å in molecule 1 and Ru(7)–Ru(8) 3.043(3) Å in molecule 2), as has been previously observed in other Ru–Sn mixed-metal clusters.^{5–9} The Ru(2)–Sn(1) (2.581(3) Å) in molecule 1 and the Ru(7)–Sn(2) (2.583(3) Å) in molecule 2 bond lengths are within the range observed previously, as in [(μ-H)₂(μ₃-S)-(μ-Cl)Ru₃(CO)₈(SnCl₃)] (Ru–Sn 2.571(1) Å),⁵ [Ru₃(μ-H)-(μ₃,η²-amphyl){μ,η¹:η²-PhC=C(H)Ph}(SnPh₃)(CO)₇] (Ru–Sn 2.662(1) Å),⁶ [Ru₃(μ-H)(μ₃,η²-amphyl){μ,η¹:η²-PhC=C(H)Ph}-(SnPh₃)(CO)₇] (different isomer, Ru–Sn 2.623(1) Å),⁶ in which a SnR₃ fragment is terminally bound to a ruthenium atom; and [Me₃Sn(CO)₃Ru(SnMe₂)₂] (Ru–Sn 2.638(2)–2.694(2) Å),⁷ [Ru₃(CO)₁₀(SnR₂)₂] (Ru–Sn 2.733(2)–2.739(2) Å),⁸ [Ru₃(CO)₉(μ-SnR'₂)₃] (Ru–Sn 2.715(2)–2.734(2) Å),⁹ [Ru₃(CO)₉(μ-SnR₂)(μ-SnR'₂)₂] (Ru–Sn 2.705(2)–2.750(2) Å),⁹ [Ru₃(CO)₉(μ-SnR₂)₂(μ-SnR'₂)] (Ru–Sn 2.641(2)–2.729(2) Å),⁹ and [Ru₂(CO)₆(μ-SnR₂)(dppm)] (Ru–Sn 2.699(1)–2.715(1) Å),⁹ in which SnR₂ fragments are bridging Ru–Ru edges. The Ru(1)–Sn(1) and the Ru(8)–Sn(2) bonds (3.140(2) and 3.102(2) Å, respectively) in **4** are much longer but still within bonding distance, implying that the SnCl₃ fragment forms an asymmetrical bridge, intermediate between the symmetrically bridging and terminal bonding modes observed in other Ru–Sn clusters.^{5–9} This confers to the tin atom a nearly perfect trigonal bipyramidal coordination geometry, with Ru(1) or Ru(8) equatorial, and Ru(2) or Ru(7) in axial position.

The IR spectrum of compound [Ru₆C(CO)₁₆SnCl₂] **2** contains CO stretching bands attributable to terminal carbonyl ligands only. Compound **2** has been characterised by positive electron impact mass spectrometry, and its spectrum consists of the parent ion at *m/z* 1256 followed by peaks corresponding to loss of CO ligands.

The molecular structure of [Ru₆C(CO)₁₆SnCl₂] **2** is shown in Fig. 2, together with selected bond lengths and angles. As with anion **4**, it consists of a Ru₆C(CO)₁₆ octahedron edge-bridged by a SnCl₂ fragment. Each ruthenium atom bears three

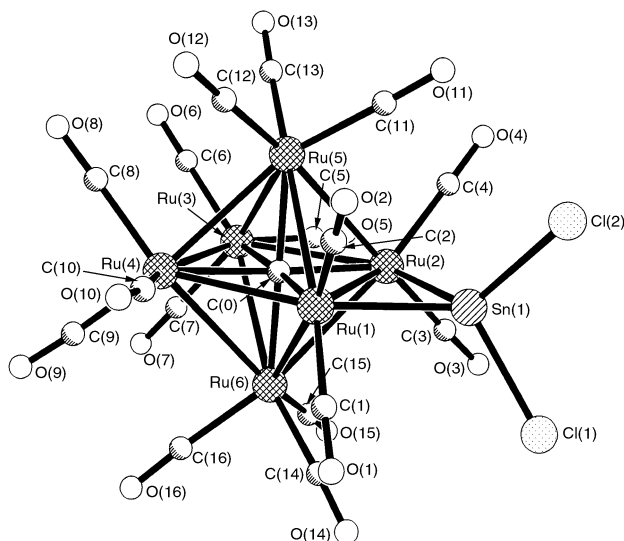


Fig. 2 Molecular structure of [Ru₆C(CO)₁₆SnCl₂] **2** with atom numbering scheme. Selected bond lengths (Å) and angles (°): Ru(1)–Sn(1) 2.5907(11), Ru(2)–Sn(1) 2.5733(12), Sn(1)–Cl(1) 2.2454(15), Sn(1)–Cl(2) 2.343(2), Ru(1)–Ru(2) 3.0559(11), Ru–Ru (mean) 2.91(2), C–O (mean) 1.131(2), Ru(1)–Sn(1)–Ru(2) 72.56(2), Cl(1)–Sn(1)–Cl(2) 100.24(6), Cl(1)–Sn(1)–Ru(1) 118.07(4), Cl(1)–Sn(1)–Ru(2) 121.54(5).

terminally bound carbonyl ligands, except for the two ruthenium atoms supporting the Sn(IV) bridge, which bear two carbonyl ligands only. The Ru₆C core remains unchanged. Again the Ru–Ru edge bearing the SnCl₂ fragment is the longest (Ru(1)–Ru(2) 3.0559(11) Å [3.039(3) Å in **4**]), with the other Ru–Ru bonds ranging from 2.8280(10) to 2.9429(10) Å [2.89(2) Å (mean) in **4**]. The Ru–Sn bonds (2.5907(11) and 2.5733(12) Å) are very similar to the shortest Ru–Sn bond in **4** (2.581(3) Å), and within the range observed in previously reported Ru–Sn clusters (2.571(1)–2.750(2) Å).^{5–9}

In this work we have demonstrated that simple derivatives of Sn(IV) containing the 'ligand' [Ru₆C(CO)₁₆]^{2–} may be readily obtained. The coordination chemistry about the central Sn(IV) ion would appear to be normal (tetrahedral or tbp). This fundamental idea has been extended to other metal systems and, for example, related derivatives of square planar Pt(II) have been obtained similarly. These new Ru–Sn clusters have been shown to be ideal precursors to catalytically active Ru–Sn nanoparticles.

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Notes and references

† We derive this oxidation state (+4) by removing the 'ligand' [Ru₆C(CO)₁₆] in its closed shell configuration, *i.e.* as [Ru₆C(CO)₁₆]^{2–}.

- D. S. Shephard, T. Maschmeyer, B. F. G. Johnson, J. M. Thomas, G. Sankar, D. Ozkaya, W. Zhou, R. D. Oldroyd and R. G. Bell, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2242.
- D. S. Shephard, T. Maschmeyer, G. Sankar, J. M. Thomas, D. Ozkaya, B. F. G. Johnson, R. Raja, R. D. Oldroyd and R. G. Bell, *Chem.-Eur. J.*, 1998, **4**, 1214.
- R. Raja, G. Sankar, S. Hermans, D. S. Shephard, S. Bromley, J. M. Thomas, B. F. G. Johnson and T. Maschmeyer, *Chem. Commun.*, 1999, 1571.
- See for example: Y. Pouilloux, F. Austin, C. Guimon and J. Barrault, *J. Catal.*, 1998, **176**, 215; Y. Moritomo and E. B. Yeager, *J. Electroanal. Chem.*, 1998, **444**, 95.
- R. D. Adams and D. A. Katahira, *Organometallics*, 1982, **1**, 53.
- J. A. Cabeza, S. Garcia-Granda, A. Llamazares, V. Riera and J. F. Van der Maelen, *Organometallics*, 1993, **12**, 157.
- S. F. Watkins, *J. Chem. Soc. A*, 1969, 1552.
- C. J. Cardin, D. J. Cardin, G. A. Lawless, J. M. Power and M. B. Power, *J. Organomet. Chem.*, 1987, **325**, 203.
- C. J. Cardin, D. J. Cardin, M. A. Convery, Z. Dauter, D. Fenske, M. M. Devereux and M. B. Power, *J. Chem. Soc., Dalton Trans.*, 1996, 1133.
- Crystallographic data:** [Ru₆C(CO)₁₆SnCl₂] **2**: C₁₇Cl₂O₁₆Ru₆Sn, *M* = 1256.18, monoclinic, *a* = 16.740(6), *b* = 16.500(7), *c* = 20.941(9) Å, β = 90.96(2)°, *U* = 5783.3(41) Å³, *T* = 180(2) K, space group C2/c, *Z* = 8, μ = 4.153 mm^{–1}, 9762 measured reflections, 5103 independent reflections (*R*_{int} = 0.0565), refinement method: full-matrix least squares on *F*², final *R*₁ = 0.0330, *wR*₂ = 0.0601 [*I* > 2σ(*I*)], *R*₁ = 0.0413, *wR*₂ = 0.0624 (all data). A final Fourier-difference electron-density synthesis revealed maximum and minimum residual electron density peaks of 1.192 and –1.164 e Å^{–3}. [PPN][Ru₆C(CO)₁₆SnCl₃] **4**: C₅₃H₃₀Cl₃NO₁₆P₂Ru₆Sn, *M* = 1830.18, monoclinic, *a* = 10.540(8), *b* = 34.655(7), *c* = 32.571(5) Å, β = 90.19(4)°, *U* = 11897(10) Å³, *T* = 200(2) K, space group P2₁/c, *Z* = 8, μ = 2.150 mm^{–1}, 18999 measured reflections, absorption correction using ψ scans (*T*_{max} = 0.994, *T*_{min} = 0.820), 18617 independent reflections (*R*_{int} = 0.0876), refinement method: full-matrix least squares on *F*², final *R*₁ = 0.0904, *wR*₂ = 0.1837 [*I* > 2σ(*I*)], *R*₁ = 0.1923, *wR*₂ = 0.2341 (all data). A final Fourier-difference electron-density synthesis revealed maximum and minimum residual electron density peaks of 1.360 and –1.397 e Å^{–3}. One of the PPh₃ groups of one of the PPN⁺ cations is disordered over two sites, and some disorder is also associated with two carbonyl ligands. Common, isotropic temperature factors were used for these disordered atoms, hence the relatively high *R*-values. CCDC 182/1750. See <http://www.rsc.org/suppdata/cc/b0/b004585n/> for crystallographic files in .cif format.
- A. Sirigu, M. Bianchi and E. Benedetti, *Chem. Commun.*, 1969, 596.