

# High yield synthesis and crystal structures of the Ru<sub>6</sub>–Sn cluster compounds [Ru<sub>6</sub>C(CO)<sub>16</sub>SnCl<sub>2</sub>] and [Ru<sub>6</sub>C(CO)<sub>16</sub>SnCl<sub>3</sub>]<sup>–</sup>

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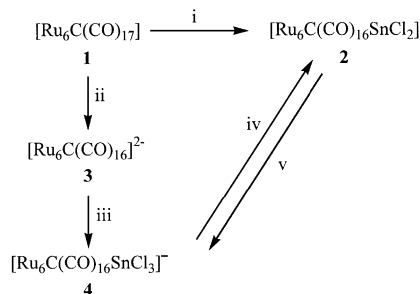
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Addition of two molar equivalents of SnCl<sub>4</sub> to [Ru<sub>6</sub>C(CO)<sub>16</sub>]<sup>2–</sup> yields first the new [Ru<sub>6</sub>C(CO)<sub>16</sub>SnCl<sub>3</sub>]<sup>–</sup> cluster anion and then [Ru<sub>6</sub>C(CO)<sub>16</sub>SnCl<sub>2</sub>], the latter being also the single product of the direct addition of SnCl<sub>2</sub> to [Ru<sub>6</sub>C(CO)<sub>17</sub>].

We are currently investigating the preparation and catalytic activity of bimetallic nanoparticles derived from fully characterised bimetallic cluster compounds.<sup>1–3</sup> 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.<sup>4</sup> However, few Ru–Sn mixed-metal clusters have been reported.<sup>5–9</sup> In this paper we report the synthesis of the new bimetallic clusters [Ru<sub>6</sub>C(CO)<sub>16</sub>SnCl<sub>2</sub>] **2** and [Ru<sub>6</sub>C(CO)<sub>16</sub>SnCl<sub>3</sub>]<sup>–</sup> **4**. We regard these new cluster species as derivatives of Sn(IV) containing formally the bidentate ligand [Ru<sub>6</sub>C(CO)<sub>16</sub>]<sup>2–</sup>.

The reaction sequence for the preparation of the compound [Ru<sub>6</sub>C(CO)<sub>16</sub>SnCl<sub>2</sub>] **2** and the anion [Ru<sub>6</sub>C(CO)<sub>16</sub>SnCl<sub>3</sub>]<sup>–</sup> **4** is outlined in Scheme 1. Direct reaction of [Ru<sub>6</sub>C(CO)<sub>17</sub>] **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 SnCl<sub>2</sub>. However, the formal oxidation state of the Sn in **2** is (IV)<sup>†</sup> indicating that a redox process of the type [Ru<sub>6</sub>C(CO)<sub>16</sub>] to [Ru<sub>6</sub>C(CO)<sub>16</sub>]<sup>2–</sup> 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 [Ru<sub>6</sub>C(CO)<sub>16</sub>]<sup>2–</sup> with stannic chloride in dichloromethane produce the same Sn(IV) cluster **2** and in addition the anion [Ru<sub>6</sub>C(CO)<sub>16</sub>SnCl<sub>3</sub>]<sup>–</sup> **4** (as its PPN<sup>+</sup> salt). Anion **4** is obtained



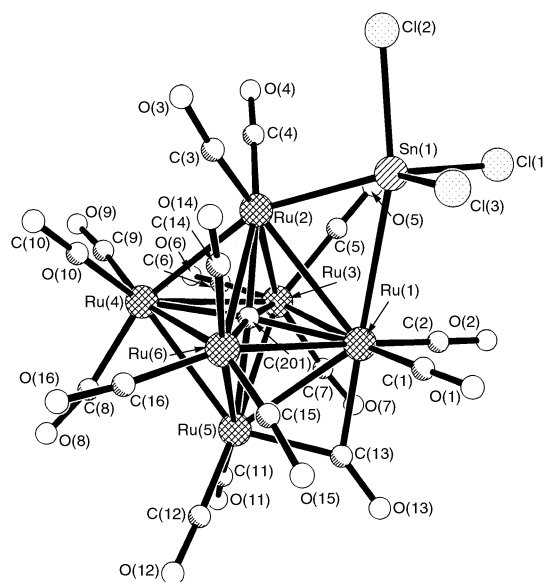
**Scheme 1** Synthesis of the cluster species [Ru<sub>6</sub>C(CO)<sub>16</sub>SnCl<sub>2</sub>] and [Ru<sub>6</sub>C(CO)<sub>16</sub>SnCl<sub>3</sub>]<sup>–</sup> **3**. *Reagents and conditions:* i, reaction with SnCl<sub>2</sub> in dichloromethane, reflux, 4 days; ii, reaction with KOH–MeOH; iii, reaction with SnCl<sub>4</sub> in dichloromethane at room temperature; iv, reaction with SnCl<sub>4</sub> in dichloromethane under reflux; v, reaction with [PPN]Cl in dichloromethane at room temperature.

in 67% yield when equimolar amounts of [Ru<sub>6</sub>C(CO)<sub>16</sub>]<sup>2–</sup> **3** and SnCl<sub>4</sub> are reacted. Treatment of **4** with further stannic chloride (1 mole) results in Cl<sup>–</sup> ion abstraction and the formation of **2**. The other product of this reaction is the Sn(IV) anion [SnCl<sub>5</sub>]<sup>–</sup>. This reaction is easily reversed, and addition of Cl<sup>–</sup> {as [PPN]Cl} to **2** results in the formation of **4**. The ease with which cluster **2** accepts the additional Cl<sup>–</sup> to generate a coordinated SnCl<sub>3</sub><sup>–</sup> group is of interest and in line with the established chemistry of SnCl<sub>4</sub>. This emphasises the view of compound **2** as an adduct of the type XSnCl<sub>2</sub>, where X = the bidentate dianionic ligand [Ru<sub>6</sub>C(CO)<sub>16</sub>]<sup>2–</sup>.

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.<sup>10</sup>

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 [Ru<sub>6</sub>C(CO)<sub>16</sub>SnCl<sub>3</sub>]. The IR spectra of **4** in the ν<sub>CO</sub> stretching region consists of peaks at 2086, 2056, 2035, 2026, 1987 and 1973 cm<sup>–1</sup> corresponding to terminal carbonyls, and a broad peak at 1825 cm<sup>–1</sup> corresponding to bridging CO.

The molecular structure of the anion [Ru<sub>6</sub>C(CO)<sub>16</sub>SnCl<sub>3</sub>]<sup>–</sup> **4** is shown in Fig. 1, together with selected bond lengths and angles. It consists of the intact core of the Ru<sub>6</sub>C(CO)<sub>16</sub> cluster, with one Ru–Ru edge bridged by a SnCl<sub>3</sub> fragment. It is



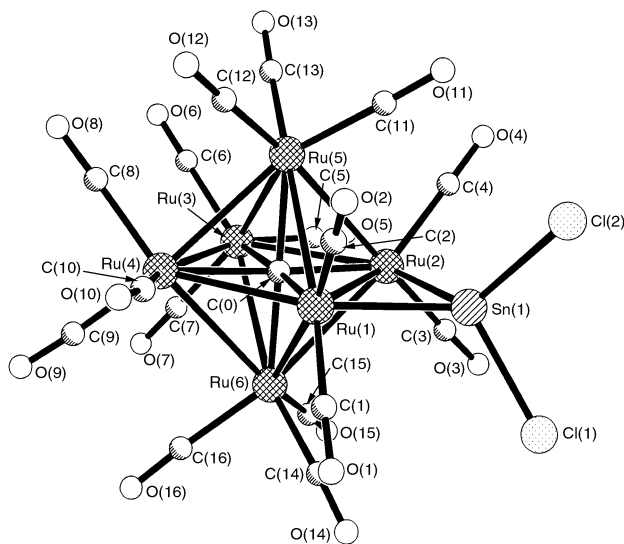
**Fig. 1** Molecular structure of [Ru<sub>6</sub>C(CO)<sub>16</sub>SnCl<sub>3</sub>]<sup>–</sup> **4** with atom numbering scheme. Selected bond lengths (Å) and angles (°): Molecule 1: Ru(1)–Sn(1) 3.140(2), Ru(2)–Sn(1) 2.581(3), Sn(1)–Cl(1) 2.391(6), Sn(1)–Cl(2) 2.459(5), Sn(1)–Cl(3) 2.406(5), Ru(1)–Ru(2) 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).

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

The geometry of the Ru<sub>6</sub>C 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 [Ru<sub>6</sub>C(CO)<sub>17</sub>].<sup>11</sup> 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.<sup>5–9</sup> 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)<sub>2</sub>(μ<sub>3</sub>-S)-(μ-Cl)Ru<sub>3</sub>(CO)<sub>8</sub>(SnCl<sub>3</sub>)] (Ru–Sn 2.571(1) Å),<sup>5</sup> [Ru<sub>3</sub>(μ-H)-(μ<sub>3</sub>,η<sup>2</sup>-amph)<sub>2</sub>]{μ,η<sup>1</sup>:η<sup>2</sup>-PhC=C(H)Ph}(SnPh<sub>3</sub>)(CO)<sub>7</sub>] (Ru–Sn 2.662(1) Å),<sup>6</sup> [Ru<sub>3</sub>(μ-H)(μ<sub>3</sub>,η<sup>2</sup>-amph){μ,η<sup>1</sup>:η<sup>2</sup>PhC=C(H)Ph}-(SnPh<sub>3</sub>)(CO)<sub>7</sub>] (different isomer, Ru–Sn 2.623(1) Å),<sup>6</sup> in which a SnR<sub>3</sub> fragment is terminally bound to a ruthenium atom; and [Me<sub>3</sub>Sn(CO)<sub>3</sub>Ru(SnMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub> (Ru–Sn 2.638(2)–2.694(2) Å),<sup>7</sup> [Ru<sub>3</sub>(CO)<sub>10</sub>(SnR<sub>2</sub>)<sub>2</sub>] (Ru–Sn 2.733(2)–2.739(2) Å),<sup>8</sup> [Ru<sub>3</sub>(CO)<sub>9</sub>(μ-SnR'<sub>2</sub>)<sub>3</sub>] (Ru–Sn 2.715(2)–2.734(2) Å),<sup>9</sup> [Ru<sub>3</sub>(CO)<sub>9</sub>(μ-SnR<sub>2</sub>)(μ-SnR'<sub>2</sub>)<sub>2</sub>] (Ru–Sn 2.705(2)–2.750(2) Å),<sup>9</sup> [Ru<sub>3</sub>(CO)<sub>9</sub>(μ-SnR<sub>2</sub>)<sub>2</sub>(μ-SnR'<sub>2</sub>)] (Ru–Sn 2.641(2)–2.729(2) Å),<sup>9</sup> and [Ru<sub>2</sub>(CO)<sub>6</sub>(μ-SnR<sub>2</sub>)(dppm)] (Ru–Sn 2.699(1)–2.715(1) Å),<sup>9</sup> in which SnR<sub>2</sub> 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 SnCl<sub>3</sub> fragment forms an asymmetrical bridge, intermediate between the symmetrically bridging and terminal bonding modes observed in other Ru–Sn clusters.<sup>5–9</sup> 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 [Ru<sub>6</sub>C(CO)<sub>16</sub>SnCl<sub>2</sub>] **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 [Ru<sub>6</sub>C(CO)<sub>16</sub>SnCl<sub>2</sub>] **2** is shown in Fig. 2, together with selected bond lengths and angles. As with anion **4**, it consists of a Ru<sub>6</sub>C(CO)<sub>16</sub> octahedron edge-bridged by a SnCl<sub>2</sub> fragment. Each ruthenium atom bears three



**Fig. 2** Molecular structure of [Ru<sub>6</sub>C(CO)<sub>16</sub>SnCl<sub>2</sub>] **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 Ru<sub>6</sub>C core remains unchanged. Again the Ru–Ru edge bearing the SnCl<sub>2</sub> 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).<sup>5–9</sup>

In this work we have demonstrated that simple derivatives of Sn(IV) containing the 'ligand' [Ru<sub>6</sub>C(CO)<sub>16</sub>]<sup>2-</sup> 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' [Ru<sub>6</sub>C(CO)<sub>16</sub>] in its closed shell configuration, *i.e.* as [Ru<sub>6</sub>C(CO)<sub>16</sub>]<sup>2-</sup>.

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