JOURNAL OF CHEMICAL RESEARCH 2004 AUGUST, 517–518 **RESEARCH PAPER** 517

The synthesis of tetrahedral clusters $SOsCo_2(CO)_9$, relevant to chiral tetrahedral clusters containing the SOsCoW core

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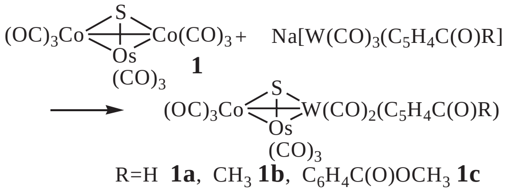
A simple route to synthesise clusters $[SOsCo_2(CO)_9]$ in excellent yield and mild reaction conditions is described. Several new chiral tetrahedral clusters containing the Os element were synthesised by the thermal reaction of the precursor $[(\mu_3\text{-}S)OsCo_2(CO)_9]$ with the functionally-substituted metal exchange reagents. The structure of cluster $[(\mu_3\text{-}S)OsCoW(CO)_8C_5H_4C(O)CH_3]$ was established by X-ray single crystal diffraction.

Keywords: osmium cluster, chiral tetrahedron, crystal structure

Mixed-metal carbonyl clusters have attracted considerable interest due to their novel structural features and interesting chemical and physical properties. They are regarded as a model system whose study can provide insight into the complicated reaction processes at catalytically active metal surfaces.[1-3] This fact, together with the hope of employing the clusters themselves in catalytic process,[4-5] especially chiral tetrahedral clusters having the potential to induce asemmetric catalytic reaction[6] has led to considerable research in this area. Studies of chiral tetrahedral clusters for enantiomers resolution and catalysis are of intense current interest, because the chirality of the cluster skeleton suggests that the framework may provide a chiral environment for catalyses. There have been relatively few studies of tetrahedral clusters containing an osmium atom, in part because it is very difficult to synthesise a tetrahedral precursor.[7] The synthesis of such precursors almost invariably involves the use of carbonyl compounds such as $[Os_3(CO)_{12}]$. Here we report a new, more convenient synthetic route for precursors using common materials under mild reaction conditions in excellent yield, and syntheses of several new complexes containing a tetrahedral skeleton, which are composed of four different elements (S, Os, Co and W).

A simple route to synthesise clusters $[SOsCo_2(CO)_9]$ has been first found in excellent yield and mild reaction conditions. The preparation of $[SOsCo_2(CO)_9]$ described in this work is illustrated in Eqn(1). This indicates that OsO_4 may easily form highly reactive $Os(CO)_3$ fragment under this reaction atmosphere, then they may be combined with $Co_2(CO)_8$ to give a tri-metal plane cluster, which can be capped by an S atom ligand and form tetrahedral clusters.[8,9] The S atom ligand in these complexes an important role to stabilise the cluster skeleton.[10] Following Eqn(1), sufficient cluster precursor can be obtained through this method to permit further studies of the reactivity of osmium atom containing clusters.



Scheme 1 Formation of clusters **1a, 1b** and **1c**

$$OsO_4 + Co_2(CO)_8 + C_4H_9SH \xrightarrow[6.0\text{-}8.0MPa]{100^oC} [SOsCo_2(CO)_9]\,90.3\% \quad (1)$$

Functionally-substituted cyclopentadienyl tricarbonyl metal anions $[W(CO)_3(\eta^5\text{-}C_5H_4)C(O)R]^-$ proved to be very important as exchange reagents in the syntheses of organometallic and metal clusters.[11,12] The exchange reagents $[W(CO)_3(\eta^5\text{-}C_5H_4)C(O)R]^-$ were formed in refluxing DMF using Na $[(\eta^5\text{-}C_5H_4)C(O)R]$ treated with $W(CO)_6$. Cluster precursor $[SOsCo_2(CO)_9]$ was treated with $Na[W(CO)_3C_5H_4C(O)R]$ in refluxing THF, afforded three new chiral tetrahedral clusters **1a**, **1b** and **1c** (summarised in Scheme 1) in a moderate yield respectively. Similar reactions have been previously reported by Vahrenkamp and others of our group.[13-15]

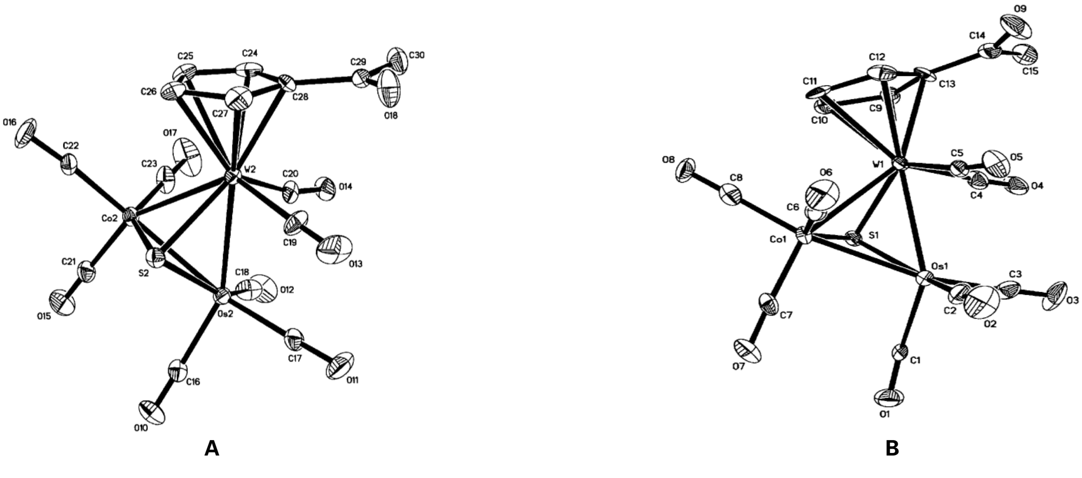


Fig. 1 Perspective view of the first and second molecular unit of the complex **1b** (**A** and **B**).

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Although complexes containing an S or Se capping atom are relatively common,[16] it is much rarer to find chiral tetrahedral clusters containing an Os atom such as those reported here. It has been proved that the $Co(CO)_3$ unit in the precursor is a good leaving group in the metal exchange reaction,[17] which can be replaced by a 15-electron group. So the three different metal tetrahedral clusters may be synthesised easily by exchange reaction using precursors. In these reactions, there was a slight amount of byproduct, which was increased by longer reaction time and not fully characterised, these air-stable clusters are black in the solid and red-purple in solution.

Clusters **1a–1c** had been characterised by element analyses, IR, ^{1}H NMR spectroscopy. In addition **1b** has been the subject of single-crystal X-ray diffraction studies, and its molecular structure is show in Fig.1

According to Fig.1, it has been proved that clusters **1a–1c** have a chiral tetrahedral skeleton-SOsCoW. All clusters showed a large number of strong terminal carbonyl absorption bands at 2079–1849cm^{-1} in their IR spectra, besides the terminal carbonyl absorption bands, there are absorption bands in the region 1821–1849cm^{-1}, which is characteristic of semi-bridging carbonyls. The higher frequency absorption bands were attributed to CO coordination on Co and Os atoms and the other to those on the W atom. The IR spectra of **1a–1c** showed corresponding C=O absorption at 1679cm^{-1} in **1a**, 1688cm^{-1} in **1b**, 1642cm^{-1} in **1c** and the IR spectrum of **1c** has another absorption band at 1723cm^{-1} attributed to ester C=O. For the ^{1}H NMR assignments of the clusters **1a–1c**, proton chemical shifts of the substituted cyclopentadienyl groups appeared downfield of the unsubstituted cyclopentadienyl, since formyl, acetyl and ester carbonyl are well known electron-withdrowing groups.[18] All protons in the cyclopentadienyl group are non-equivalent; their ^{1}H NMR spectra showed four singlets at least partly because of the chirality of the cluster skeleton. The structure of **1b** expectedly reveals the presence of two isomeric molecules in the unit cell, which are respectively in Fig.1 (A and B). The two independent molecular units are almost identical, and the very slight structural differences between them are merely reflecting the influence of packing forces. The capping S atom is bonded to Os, Co and W with bond lengths 2.337(4)Å, 2.213(4)Å and 2.368(3)Å respectively. The Mo atom is coordinated by two carbonyls and one functionally-substituted cyclopentadienyl ligand, and the Os and Co atoms are bonded by three carbonyls respectively. The averaged distance from W atom to Cp ring centre is 2.30(15) Å. The angles of C(1)–Os–C(2), C(2)–Os–C(3) and C(1)–Os–C(3) are 93.8(8)°, 91.8(8)° and 93.1(8)° respectively, which indicates that the carbonyls on the Os atom are vertical to each other. The OsCoW core in **1b** represents a scalene driangle Os(1)–Co(1) 2.644(4)Å, Os(1)–W(1) 2.8676(8)Å, W(1)–Co(1) 2.7501(18)Å, Os(2)–Co(2) 2.6333(19)Å, Os(2)–W(2) 2.8577(8)Å, W(2)–Co(2) 2.7411(18)Å. The acute angles in tetrahedral geometry of **1b** about the basal atoms range from 50.20 to 64.60°, The S atom is in a highly distorted tetrahedral environment, with an average internal M–S–M angle of 73.26°, as is typical for a capping sulfur group. The S–Os separation of 2.337(4)Å is markedly longer than that of the S–Os bond length, but is typical of a σ-bonded S–Os distance.

Experimental

Preparation of cluster **1**

Into a 100ml autoclave in a dry nitrogen atmosphere was added, OsO_4 1g(3.93mmol), $Co_2(CO)_8$ 1.5g(4.38mmol) and C_4H_9SH 0.45ml in MeOH/hexane (60ml). After assembly, the autoclave was purged twice with 4.0 MPa CO and pressurised to 7.0 MPa. The autoclave then was heated with stirring to 100°C and maintained there for 8h. After the autoclave had cooled to room temperature, it was vented slowly and the reaction mixture was carefully transited and the product was chromatographed on a 2.5×40cm silica gel column using CH_2Cl_2/hexane(2:1) as eluent. The purple-red band was the main product. After solvent was removed under vacuum, the cluster **1** was obtained (yield 90.3%).

*Preparation of clusters **1a, 1b** and **1c***: All reactions were carried out under a highly pure dinitrogen atmosphere using standard Schlenk and vacuum techniques. Petroleum ether was distilled over sodium-benzophenone while CH_2Cl_2 was distilled over CaH_2. Column chromatography was carried out using 160–200 mesh silica gel. $[W(CO)_6]$ were purchased from Fluka Chem.Co. IR spectra were recorded on a Nicolet FT-IR 10 DX spectrometer; ^{1}H NMR spectra on a Bruker AM-400 MHz spectrometer and analyses (C, H) were performed on an 1106-type analyser

*Preparation of cluster **1a***: $[W(CO)_6]$ 0.15g (0.44mmol) was added to a solution of sodium formylcyclopentadienyl NaCpCHO 0.13g (1.1mmol) in DMF 30ml. The mixture was refluxed for 4 h and cooled to room temperature. Then 0.25g(0.42mmol) of cluster $[SOsCo_2(CO)_9]$ **1** was added and then the mixture was stirred at 65°C for 4h. The solvent was removed under vacuum, the residue was extracted by the minimum amount of CH_2Cl_2 and the products were chromatographed on a 2.5×40cm silica gel column using CH_2Cl_2/hexane(2:1) as eluent. The purple-red band was the main product, the rest were the unreacted material and a slight by-product (uncharacterised). After solvent was removed under vacuum, the black solid cluster **1a** was obtained (0.16g, yield 48.5%). Anal. Calcd for **1a** $C_{14}H_5O_9OsCoWS$: C, 21.43%; H, 0.64%. Found: C, 21.23%; H, 0.65%. IR(KBr disk):(νCO)2078s, 2038s 1989s, 1897mcm^{-1}; (CHO) 1697scm^{-1}. ^{1}H NMR (TMS, $CDCl_3$) δ5.67, 5.76, 5.81, 5.92 (q, 4H, C_5H_4); δ9.64 (s, 1H, CHO).

*Preparation of cluster **1b***: The workup for **1b** was similar to that of the preparation of cluster **1a**. 0.14g(1.1mmol) $Na[CpC(O)CH_3]$ was used. The cluster **1b** was obtained (0.18g, yield 52.3%). Anal. Calcd for **3** $C_{15}H_7O_9OsCoWS$: C, 22.63%; H, 0.89%. Found: C, 22.35%; H, 0.87%. IR(KBr disk): (νCO)2079s, 2045s, 1997s, 1966s, 1902s, 1865m cm^{-1}; (C=O) 1688 cm^{-1}. ^{1}H NMR (TMS, $CDCl_3$) δ5.69, 5.77, 5.83, 5.91 (q, 4H, C_5H_4); δ2.41 (s, 3H, CH_3).

*Preparation of cluster **1c***: The workup for **1c** was similar to that of the preparation of cluster **1a**. 0.28g (1.1mmol) $Na[CpC(O)C_6H_4C(O)OCH_3]$ was used. The cluster **1c** was obtained (0.16g, yield 42.8%). Anal. Calcd for **1c** $C_{22}H_{11}O_{11}OsCoWS$: C, 28.84%; H, 1.21%. Found: C, 28.85%; H, 1.28%. IR(KBr disk): (νCO)2079, 2037, 1998, 1904cm^{-1}; (C=O) 1642, 1723cm^{-1}; (C_6H_4) 2952w, 2924w cm^{-1}. ^{1}H NMR (TMS, $CDCl_3$) δ5.66, 5.73, 5.96, 6.07 (q, 4H, C_5H_4); 2.64 (s, 3H, CH_3); δ7.85, 7.89, 8.16 (t, 4H C_6H_4).

Received 26 March 2004; accepted 29 June 2004
Paper 04/2403

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