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Preliminary Communication

Synthesis and structure of $Ir_4Sn_3(CO)_6\{CH(SiMe_3)_2\}_5O_3$; a heterometallic 'raft' with sail hoisted! *

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Abstract

Heterometallic raft clusters have been obtained previously for a variety of metals but none for tin and iridium, and more significantly none to date have had metal groups bonded above the raft plane. We report a hexametallic Ir_4Sn_2 raft to which a third tin group is attached by a single short Ir–Sn bond and three Ir–O–Sn bridges.

There is much current interest in the interface between Main Group and Transition Metal cluster chemistry [1]. By employing the low valent tin-reagent $[SnR^1_2]$ $[R^1 = CH(SiMe_3)_2]$ we sought to prepare the first tin–iridium clusters. This tin reagent, first prepared and characterised by Lappert and his co-workers [2], proved valuable in the preparation of mixed metal cluster of iron, ruthenium, and osmium having a variety of frameworks [3].

We have now studied the reactions of several tin(II) reagents SnR_2 (including $R = R^1$, or 2,4,6-triisopropylphenyl) with $[Ir_4(CO)_{11}Br]^-$, a labile derivative of the insoluble and rather unreactive parent $[Ir_4(CO)_{12}]$. We have isolated and characterised a variety of Ir–Sn clusters with nuclearities varying from 5 to 9 [4].

With strict exclusion of air and moisture $[NEt_4][Ir_4(CO)_{11}Br]$ was suspended in degassed Et_2O and a solution of $[SnR^1_2]$ in Et_2O was added. The mixture was allowed to warm to ambient temperature, stirred for 8 h, filtered to remove small amounts of $[Ir_4(CO)_{12}]$, and concentrated to *ca.* 30 ml; TLC of the product (silica; eluant hexane) showed the presence of four compounds with R_f values of 0.75, 0.65, 0.6 and 0.4. Solvent was removed under vacuum, the residue redissolved in the minimum of hexane and placed on a flash silica column under pure hexane. The first three products were collected with hexane as eluant, and gradual increase of the polarity (to *ca.* 80 : 20 hexane : dichloromethane) afforded the slowest moving species as a green solution. Evaporation of the solvent, followed by crystallisation of the residue from hexane/toluene, afforded the dark green-black crystals of the fourth product (variable yield 15–35%), suitable for an X-ray diffraction study. The samples gave a satisfactory elemental analysis; IR (KBr) ν(CO) 2064m, 2031s, 2020sh, 2008m, 1998w, 1982m, and 1976sh cm^{-1}. Suitable crystals of approximate dimensions $0.25 \times 0.15 \times 0.15$ mm were mounted on an Enraf-Nonius CAD4 diffractometer, and data were taken from 2 separate crystals owing to substantial decomposition occurring during data collection. Crystals became black and opaque following exposure, probably associated with metal–metal bond fission during X-ray exposure.

The three products which were eluted first were identified as Ir_3 and Ir_4 clusters having bridging SnR^1_2 groups [4]. Of particular interest is the fourth product, obtained as a dark green cluster of stoichiometry $[Ir_4Sn_3(CO)_6R^1_5O_3]$. The yield of this species is variable, but the highest yields were when a substantial excess of $[SnR^1_2]$ was used. Figure 1 shows the molecular structure of the molecule, which can be described as a hexametallic Ir_4Sn_2 planar 'raft' [5], surmounted by a μ_4-R^1SnO_3 'sail'. Although molecular rafts of 6 and more metal atoms are known [5] none has been reported to date with a capping group.

The geometry about the capping tin of the sail is that of a highly distorted trigonal bipyramid, with normal Sn–O distances, though it is noteworthy that the Ir–Sn distance for the sail is the shortest such separation in the cluster. It may be mentioned that structures involving Group 14 element–O–Os bonds have been postulated in deposits of osmium clusters on silica [6]. The incorporation of oxygen atoms in the reactions we describe is unique, though it is probable that they come from the silica used in chromatography. Thus, the

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* Dedicated to Professor M.F. Lappert on the occasion of his 65th birthday, with our warmest good wishes for the future.

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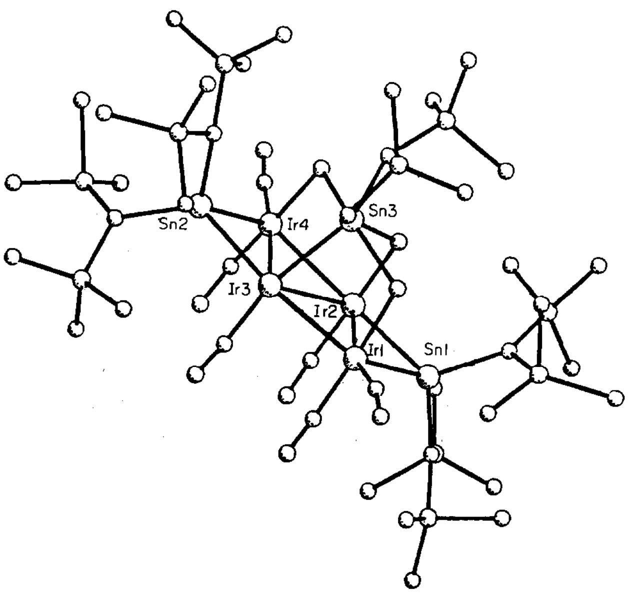

Fig. 1. A single molecule of the cluster. Selected bond lengths (Å) and angles (°): Sn(3)–Ir(3) 2.637(6), Sn(2)–Ir(3) 2.676(6), Sn(2)–Ir(4) 2.680(6), Sn(3)–O 2.008(26), 2.192(24), and 2.194(25), (to the three O-atoms); Ir–O distances 2.120(26), 2.134(25), and 2.130(26); Ir(3)–Sn(3)–C(11) 150.1(11).

product from chromatography is not the dark green species initially obtained from the reaction (IR data) [7], and reaction with $[SnAr_2]$ (Ar = 2,4,6-triisopropylphenyl) gives a similar product distribution, in which the analogous green compound observed decomposes on a silica column, precluding isolation. There is precedent for a cluster having a SnR^1 ligand [8], formed by an unusual rearrangement reaction, and having a unique framework geometry, but in that case, the bonding to the transition metal framework is by two Sn–Os bonds.

A single cluster has previously been reported bearing an SnR^1 substituent, also formed by rearrangement and having an unusual framework geometry [7*].

Crystal data: $C_{41}H_{95}Ir_4O_9Si_{10}Sn_3 \cdot C_7H_8$, $M = 2230.23$, space group $P\bar{1}$. Triclinic, $a = 12.095(9)$, $b = 15.511(11)$, $c = 22.51(2)$ Å, $\alpha = 82.48(5)$, $\beta = 87.86(5)$, $\gamma = 75.56(6)°$; $U = 4054(5)$ Å^3. $Z = 2$; $D_{calc} = 1.83$ g cm^{-3}. A total of 8307 reflections were measured to a maximum θ of 20°, using Mo-Kα radiation, with a graphite monochromator on a CAD-4 diffractometer ($\lambda = 0.71069$ Å). Data were corrected for both decay and absorption, using a linear decay correction, and empirical absorption correction (merging $R = 6.05\%$). A second crystal was mounted when the first had decayed to 60% of the initial intensity. Merging of the two datasets gave 6695 independent reflections of which 5211 were observed using the criterion $|F_o| > 4\sigma(F_o)$. The structure was solved using SHELXS (courtesy of Professor G.M. Sheldrick, University of Göttingen), and refined using full-matrix least squares (SHELX-76) to a conventional R-factor of 8.8%. The moderate quality of the data is due to serious absorption and decay problems. An absorption correction using ψ-scan data was attempted, but not used, as it made no detectable improvement in the fit to the data. The data have been deposited with the Cambridge Crystallographic Data Centre.

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References and notes

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* Reference number with asterisk indicates a note in the list of references.