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Transformation of the Incomplete Cubane-Type $Ir_3S(SH)_3$ Cluster into Single-Cubane (Ir_3SbS_4), Corner-Shared Double-Cubane (Ir_6BiS_8), and Cuboidal ($Ir_3PdS_3(SH)$) Heterometallic Clusters

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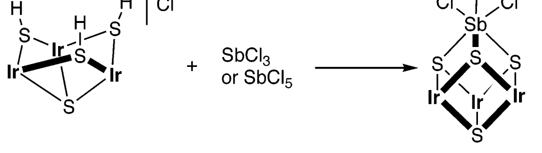
Summary: The incomplete cubane-type sulfido−hydrosulfido cluster $[(Cp^*Ir)_3(\mu_3\text{-}S)(\mu_2\text{-}SH)_3]Cl$ reacts with $SbCl_n$ ($n = 5, 3$), $BiCl_3/NEt_3$, and $Pd(PPh_3)_4$ to give the heterobimetallic sulfido clusters $[(Cp^*Ir)_3SbCl_3(\mu_3\text{-}S)_4]$, $[\{(Cp^*Ir)_3(\mu_3\text{-}S)_4\}_2Bi]Cl$, and $[(Cp^*Ir)_3PdCl(PPh_3)(\mu_3\text{-}S)_3(\mu_2\text{-}SH)]$, having a single-cubane-type core, a corner-shared double-cubane-type core, and a cuboidal core, respectively.

Transition-metal−sulfido cubane-type clusters have been attracting much attention because of their possible relevance to the active sites of certain biological and industrial catalysts as well as the building blocks of some high-performance materials. To prepare a variety of cubane-type clusters, rational methods to construct the cores with the desired metal composition have been explored extensively.[1] Among several reactions exploited to date, treatment of the incomplete cubane-type aqua clusters $[M_3S_4(H_2O)_9]^{4+}$ (M = Mo, W) with a series of transition metals and main-group metals M′ or their salts has turned out to be extremely versatile, since it readily affords a variety of mixed-metal clusters containing the $M'M_3S_4$ core.[2] Quite recently the chemistry of this Mo cluster has been extended to that of the organometallic analogue $[(Cp'Mo)_3S_4]^+$ ($Cp' = \eta^5\text{-}C_5H_4\text{-}Me$,[3] $\eta^5\text{-}C_5Me_5$ (Cp*)[4]) and several mixed-metal clusters have been synthesized. In a previous paper,[5] we reported the synthesis and full characterization of the incomplete cubane-type sulfido−hydrosulfido cluster $[(Cp^*Ir)_3(\mu_3\text{-}S)(\mu_2\text{-}SH)_3]Cl$ (**1**). We have found that **1** can serve as a good starting compound for the construction of a new series of heterometallic $M'Ir_3S_4$ cubane-type cores, as described below.

Treatment of **1** with a slight excess of $SbCl_5$ in CH_2Cl_2 at room emperature afforded the single-cubane-type cluster $[(Cp^*Ir)_3SbCl_3(\mu_3\text{-}S)_4]$ (**2**) with a formal $Ir^{III}{}_3Sb^V$ core, which was isolated as purple crystals in 61% yield. Also from the reaction of **1** with an equimolar or slight excess of $SbCl_3$ in THF at room temperature, **2** was obtained as the only characterizable product in 32% yield (eq 1).[6] In the latter reaction, the fate of the hydrosulfido protons in **1** is unknown, and the stoichiometry for generating the formal Sb^V center from $SbCl_3$ is not certain. An X-ray analysis using a single crystal of $\mathbf{2}\cdot CH_2Cl_2$ has demonstrated unambiguously the formation of the cubane-type core having a mirror plane defined by Ir(1), Sb(1), S(2), and S(1) atoms (Figure 1a).[7] The Ir_3Sb tetrahedral core is distorted only slightly, with almost identical intermetallic distances at 3.579(2), 3.556(3), 3.581(3), and 3.555(2) Å for the Ir(1)−Ir(2), Ir(2)−Ir(2*), Ir(1)−Sb, and Ir(2)−Sb edges, respectively, which are indicative of the absence of any metal−metal bonding interactions.



(1)

1 **Ir** = Cp*Ir **2**

From the reaction of **1** with 1 equiv of $BiCl_3$ under similar conditions, formation of a cluster containing a $\{(Cp^*Ir)_3(\mu_3\text{-}S)_4\}_2Bi$ core was suggested by preliminary X-ray analysis, but full characterization of this product was not successful. When the reaction was carried out in the presence of excess NEt_3 (5 equiv), the well-defined, corner-shared, double-cubane-type cluster $[\{(Cp^*Ir)_3(\mu_3\text{-}S)_4\}_2Bi]Cl$ (**3**) with a formal $Ir^{III}{}_6Bi^V$ core was isolated as dark green crystals, in a yield of 19% based on **1** (eq 2).[8] Oxidation of Bi^{III} to Bi^V took place

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[6] (a) Into a CH_2Cl_2 solution (5 mL) of **1** (57 mg, 50 μmol) was added $SbCl_5$ (7.0 μL, 55 μmol), and the mixture was stirred at room temperature for 11 h. The resulting purple mixture was filtered, and hexane was added to the filtrate, affording $\mathbf{2}\cdot CH_2Cl_2$ (43 mg, 61% yield). (b) A mixture containing **1** (57 mg, 50 μmol) and $SbCl_3$ (18 mg, 79 μmol) in THF (5 mL) was stirred at room temperature for 24 h. The resulting red-purple mixture was filtered, and the filtrate was dried in vacuo. Crystallization of the residue from CH_2Cl_2−hexane afforded $\mathbf{2}\cdot CH_2Cl_2$ (23 mg, 32% yield based on **1**). ^1H NMR ($CDCl_3$): δ 1.62 (s, 45H, Cp*), 5.30 (s, 2H, CH_2Cl_2). Anal. Calcd for $C_{31}H_{47}Cl_5S_4Ir_3Sb$: C, 26.15; H, 3.33. Found: C, 26.05; H, 3.29.

[7] Crystal data for $\mathbf{2}\cdot CH_2Cl_2$, $C_{31}H_{47}S_4Cl_5Ir_3Sb$: monoclinic, space group $P2_1/m$ (No. 11), $a = 10.440(8)$ Å, $b = 17.64(1)$ Å, $c = 11.287(6)$ Å, $\beta = 97.50(5)°$, $V = 2061(3)$ Å^3, $Z = 2$, μ(Mo Kα) = 108.76 cm^{-1}, room temperature, $R1 = 0.054$ and $wR2 = 0.129$ for 3818 unique reflections with $I > 3.00\sigma(I)$ and 195 variables.

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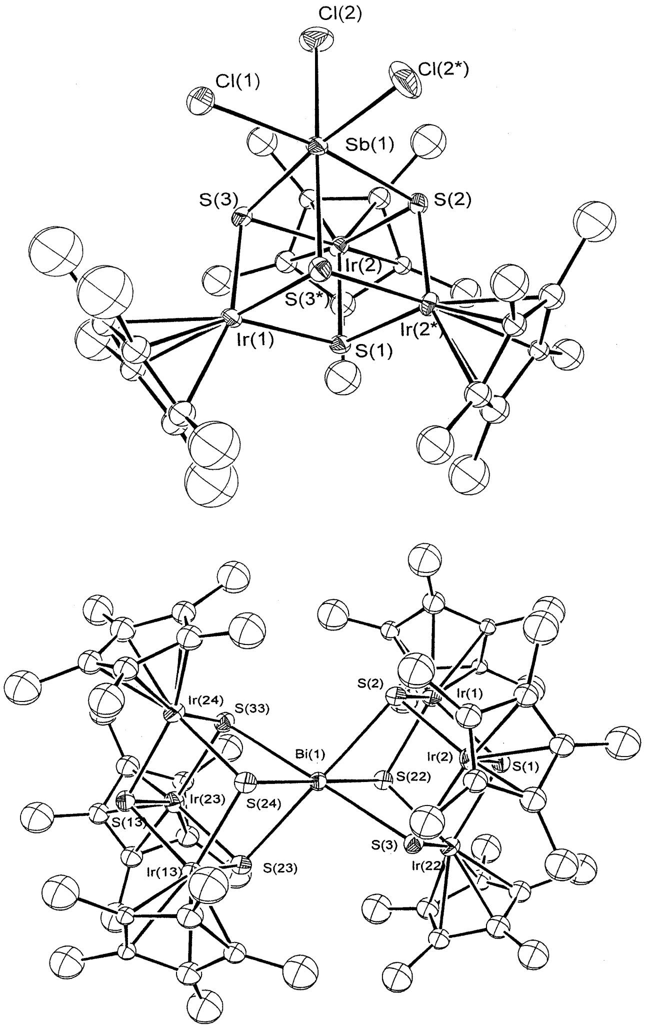
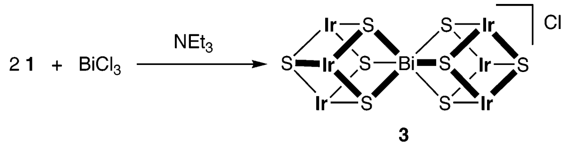


Figure 1. ORTEP drawings for **2** (a, top) and the cation of **3** (b, bottom). Hydrogen atoms are omitted for clarity. Selected bonding parameters for **2** (bond lengths in Å and angles in deg): Ir−S = 2.333(3)−2.378(4), Sb−S(2) = 2.552(4), Sb−S(3) = 2.546(3); S−Ir−S = 80.9(1)−90.6(1), S(2)−Sb(1)−S(3) = 81.3(1), S(3)−Sb−S(3*) = 81.1(2). Selected bonding parameters for **3** (bond lengths in Å and angles in deg): Bi−S(2) = 2.671(3), Bi−S(3) = 2.677(4), Ir−S = 2.353(3)−2.384(4); S(2)−Bi−S(3) = 78.43(10), S(2)−Bi−S(22) = 78.5(1), S−Ir−S = 80.8(1)−91.8(1).

similarly, but the stoichiometry of this reaction is uncertain. Although treatment of **1** with 0.5 equiv of $BiCl_3$ also gave **3**, the yield was not improved. It is to



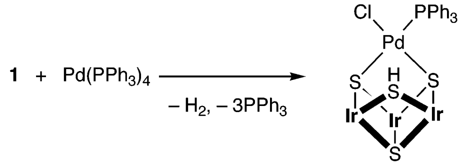
3

(2)

be noted that treatment of **1** with $SbCl_3$ in the presence of NEt_3 produced only the single-cubane-type cluster **2** in essentially the same yield as that from the reaction without NEt_3. Cluster **3** was characterized crystallographically as shown in Figure 1b;[9] the molecule has an inversion center at Bi along with a mirror plane consisting of Bi, Ir(1), S(1), and S(3). Due to the covalent radius of Bi being larger than that of Sb, the Bi−S bond lengths (2.671(3) and 2.677(4) Å) are significantly larger than the Sb−S bond distances in **2** (2.552(4) and 2.546(3) Å), whereas the Ir−S bonds in the range 2.35−2.39 Å for **3** are comparable to those for **2** (2.33−2.38 Å). Accordingly, the $BiIr_3$ tetrahedron in **3** is considerably more distorted than the $SbIr_3$ core in **2**; the Bi−Ir(1) and Bi−Ir(2) separations of 3.678(2) and 3.6830(10) Å are somewhat longer than the Ir(1)−Ir(2) and Ir(2)−Ir(22) distances of 3.6030(10) and 3.607(2) Å.

Incorporation of Sb[10,11] and Bi[11] into the incomplete cubane-type Mo_3S_4 aqua cluster $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(H_2O)_9]^{4+}$ has been reported previously, with the corner-shared double-cubane-type cluster $[\{Mo_3(\mu_3\text{-}S)_4(H_2O)_9\}_2M']^{8+}$ (M′ = Sb, Bi) being formed exclusively. The selenido clusters $[M_3Se_4(H_2O)_9]^{4+}$ (M = Mo, W) are also known to afford only the corner-shared double cubanes.[12] It is therefore of interest that in the present study the structures of the products obtained from **1** with $SbCl_3$ and $BiCl_3$ are not identical. Although incorporation of further different heterometals into the Mo_3S_4 aqua cluster has been reported, there is no precedent for a reaction in which metals in the same triad afford clusters with different core types. In the present case, it is possible that the smaller covalent radius of Sb compared to that of Bi precludes the formation of the corner-shared double-cubane core due to stronger steric repulsion between the bulky Cp* ligands.

It has been found that **1** also reacts with equimolar $Pd(PPh_3)_4$ in THF at room temperature to give a cluster as black crystals in 54% yield, which was characterized to be $[(Cp^*Ir)_3PdCl(PPh_3)(\mu_3\text{-}S)_3(\mu_2\text{-}SH)]$ (**4**) by X-ray diffraction as well as spectroscopic data (eq 3).[13] Concomitant evolution of H_2 gas was confirmed (1.0 mol/mol of **1**). The reaction carried out in the presence of



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(3)

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(8) A mixture containing **1** (57 mg, 50 μmol), $BiCl_3$ (16 mg, 50 μmol), and NEt_3 (35 μL, 250 μmmol) in THF (5 mL) was stirred at room temperature for 24 h. The resulting dark green mixture was filtered, and the filtrate was dried in vacuo. Crystallization of the residue from CH_2Cl_2−hexane afforded $\mathbf{3}\cdot CH_2Cl_2$ (12 mg, 19% yield based on **1**). ^1H NMR ($CDCl_3$): δ 1.61 (s, 90H, Cp*), 5.30 (s, 2H, CH_2Cl_2). Anal. Calcd for $C_{61}H_{92}Cl_3S_8Ir_6Bi$: C, 28.73; H, 3.64. Found: C, 28.36; H, 3.99.

(9) Crystal data for $\mathbf{3}\cdot CH_2Cl_2$, $C_{61}H_{92}S_8Cl_3Ir_6Bi$: monoclinic, space group *C*2/*m* (No. 12), a = 17.350(8) Å, b = 18.948(8) Å, c = 12.867(6) Å, β = 121.146(4)°, V = 3620(3) Å^3, Z = 2, μ(Mo Kα) = 138.08 cm^{-1}, room temperature, $R1$ = 0.042 and w$R2$ = 0.106 for 2555 unique reflections with $I > 3.00\sigma(I)$ and 185 variables.

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(13) A mixture containing **1** (57 mg, 50 μmol) and $Pd(PPh_3)_4$ (56 mg, 49 μmol) in THF (5 mL) was stirred at room temperature for 24 h. The resulting black mixture was filtered. Addition of hexane to the concentrated filtrate afforded $\mathbf{4}\cdot$2THF (44 mg, 54% yield). ^1H NMR (C_6D_6): δ 1.40 (s, 15H, Cp*, and 8H, OCH_2CH_2 in THF), 1.64, 1.73 (s, 15H each, Cp*), 3.57 (8H, OCH_2 in THF), 4.77 (s, 1H, SH), 7.98 (m, 15H, PPh). IR (KBr): 2242 cm^{-1} (SH). Anal. Calcd for $C_{56}H_{77}O_2ClPS_4Ir_3Pd$: C, 40.52; H, 4.68. Found: C, 40.31; H, 4.67. Crystal data for $\mathbf{4}\cdot$2THF, $C_{56}H_{77}O_2PS_4ClIr_3Pd$: triclinic, space group $P\bar{1}$ (No. 2), a = 12.334(4) Å, b = 12.433(2) Å, c = 21.043(4) Å, α = 99.62(1)°, β = 106.28(2)°, γ = 100.45(2)°, V = 2964(1) Å^3, Z = 2, μ(Mo Kα) = 72.82 cm^{-1}, room temperature, $R1$ = 0.044 and w$R2$ = 0.111 for 10 055 unique reflections with $I > 3.00\sigma(I)$ and 665 variables.

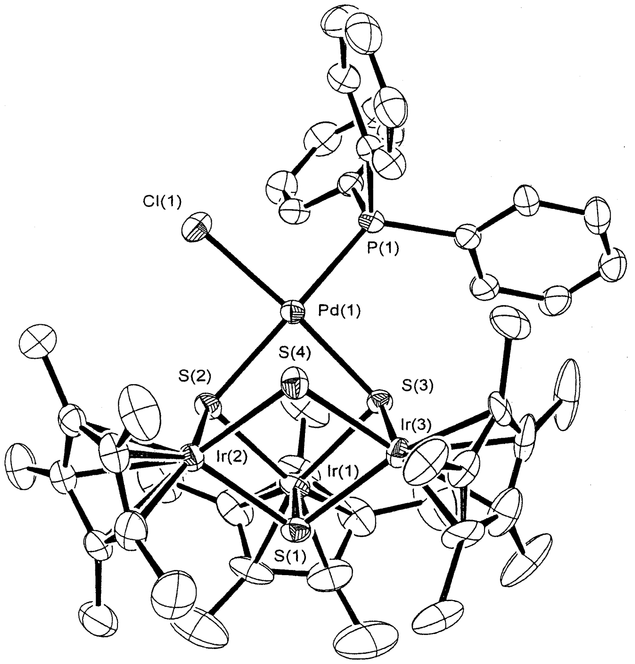

Figure 2. ORTEP drawing for **4**. Hydrogen atoms are omitted for clarity. Selected bonding parameters (bond lengths in Å and angles in deg): Pd(1)−S(2) = 2.311(2), Pd(1)−S(3) = 2.339(2), Ir−S = 2.349(2)−2.388(2); S(2)−Pd−S(3) = 83.63(8), S−Ir−S 79.51(8)−92.60(8).

excess NEt_3 also gave **4**, where the formation of the cubane core $Ir_3Pd(\mu_3\text{-}S)_4$ through dehydrochlorination was not observed. As shown in Figure 2, **4** has a cuboidal core, in which the Pd is bonded to only two sulfido atoms. Thus, the core comprises three Ir atoms, one square-planar Pd atom, three μ_3-sulfides, and one μ_2-hydrosulfide (S(4)). The Ir_3Pd tetrahedron is greatly distorted, with the longer Ir(2)−Pd(1) and Ir(3)−Pd(1) distances at 3.961(1) and 3.917(1) Å as compared to the other four metal−metal separations (3.36−3.60 Å). It is interesting to note that the $Mo_3Pd(\mu_3\text{-}S)_4$ clusters $[\{Mo(L)\}_3PdCl(\mu_3\text{-}S)_4]^{3+}$ (L = 1,4,7-triazacyclononane) and $[\{Mo(H_2O)_3\}_6Pd_2(\mu_3\text{-}S)_6(\mu_4\text{-}S)_2]^{8+}$ [14] derivable from $[Mo_3(\mu_3\ S)(\mu_2\text{-}S)_3(H_2O)_9]^{4+}$ as well as $[(Cp'Mo)_3Pd(PPh_3)(\mu_3\text{-}S)_4]^{+}$ [3,4] from $[(Cp'Mo)_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3]^{+}$ contain the cubane-type core with a tetrahedral Pd site. In these Mo_3PdS_4 clusters, due to the presence of the high-valent, electron-deficient Mo centers, all metal−metal separations (2.75−2.84 Å) fall in the range of those expected for metal−metal bonding interactions. This contrasts with **4**, which contains Ir centers that obey the 18-electron count without any metal−metal bonds. Further studies are now in progress to clarify the reactivities of **1** toward a wider range of transition-metal and main-group-metal compounds.

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Supporting Information Available: Tables of crystallographic data for **2**·CH_2Cl_2, **3**·CH_2Cl_2, and **4**·2THF. This material is available free of charge via the Internet at http://pubs.acs.org.

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