clusters, $(Et_3P)_6M_6X_8$ (M = Co, X = S,[7] Se;[8] M = Fe,[9] Mo,[10] W,[11] X = S). Comparison of this structure to the sulfur and selenium analogues verifies the conclusion advanced by Zanello[12] that bonding in the cobalt clusters is dominated by the cobalt–chalcogen bonds. The large Co–Co and Te–Te separations preclude significant metal–metal or chalcogen–chalcogen bonding. As expected on the basis of atomic sizes the Co/Te cluster is larger than the corresponding Co/S and Co/Se clusters. (We have isolated ions of the $(Et_3P)_6Co_6Te_8$ cluster, and will report their syntheses and characterizations separately.)

We examined the thermal behavior of **1** by differential scanning calorimetry (DSC). This showed a broad endotherm between approximately 225 and 275 °C. In order to determine the source of this endotherm, we conducted the thermolysis on a preparative scale and found that heating **1** in a sealed tube to 300 °C for 45 min gives polycrystalline β-CoTe.[13] This molecule-based preparation of the solid is summarized in eq 1.

$$3Co_2(CO)_8 + 8TePEt_3 \xrightarrow[-PEt_3]{-CO} Co_6Te_8(PEt_3)_6 \xrightarrow[-PEt_3]{\Delta} \beta\text{-CoTe} \qquad (1)$$

It is important to see if there is any structural relationship between compound **1** and the solid product CoTe, for at least two reasons. First, it will help elucidate the chemical processes by which molecular starting materials are converted to solid-state products. Second, when studying the particle-size dependence of properties of a solid,[14] one must know at what point a molecule is of the right size and shape to be considered a small piece of a solid. We can identify the Co_6Te_8 nucleus of **1** as a reconstructed fragment of bulk CoTe in the following way.

Cobalt telluride, $Co_{1-x}Te$, forms in the NiAs structure over a wide range of x. The NiAs structure consists of an hexagonal close-packed array of anions with cations filling the octahedral holes in the anion lattice.[15] A complementary description of the structure is the regular combination of three sites: the anion, the cation, and the remaining interstitial void. Each anion in the lattice is at the center of a trigonal prism of cations; each cation is at the center of an octahedron of anions, and each interstitial site is defined equivalently by either a second trigonal prism of cations or by a trigonal bipyramid of anions. (Occupation of this site gives the "filled NiAs structure"—the Ni_2In structure type[16]). Figure 2a shows a drawing of this interstitial site.

To arrive at the structure in Figure 2a, we included the void site and its first and second nearest neighbors. This gives the formula Co_6Te_8. For comparison the Co_6Te_8 core of **1** is shown in Figure 2b. These figures show that the CoTe fragment results from a 60° twist of one face of the Co_6 octahedron of **1**, thereby generating a Co_6 trigonal prism. In conjunction with this, the six Te atoms involved in the twist reorganize; three cap the rectangular faces of the trigonal prism, and three span the vertical edges of the prism.

This analysis shows that **1** can be viewed as a small, distorted fragment of the CoTe structure. While the reorganization that connects the two structures in Figure 2 is qualitatively drastic, it is conceptually simple. Comparison of the two structures hints at the pathway the molecular reagents, cobalt carbonyl, and the phosphine telluride take to get to the solid product and shows some of the reconstruction CoTe can undergo as the particle size becomes very small. We are studying the reactions which lead to **1** and from **1** to other CoTe clusters in order to further characterize the molecules-to-solids transformation.

It is interesting to note in passing that there is such a relationship between the NiAs structure and the M_6X_8 cluster that is the building block of the Chevrel phases.

Acknowledgment. We gratefully acknowledge P. Trevor for X-ray fluorescence measurements.

Supplementary Material Available: Tables listing crystallographic data, positional and thermal parameters, and significant distances and angles for $(Et_3P)_6Co_6Te_8$, a diagram showing the packing of **1** in the crystal, and a DSC trace of the thermal behavior of **1** (10 pages); a table of calculated and observed structure factors (52 pages). Ordering information is given on any current masthead page.

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(13) Compound **1** (400 mg; 0.19 mmol) was sealed in Pyrex under vacuum and heated in a tube furnace at 300 °C for 45 min. This gave triethylphosphine and a shiny black solid. The tube was cooled and the solid was collected, washed with pentane, and dried (yield = 264 mg = 100% based on the second reaction in eq 1). Powder X-ray diffraction shows only β-CoTe. Anal. (Analytische Laboratorien). Found (calcd for $Co_{0.75}Te$): C, 0.60 (0.0); H, 0.03 (0.0); P, 0.88 (0.0); Co, 25.15 (25.73); Te, 70.60 (74.27).

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High-Nuclearity Platinum–Osmium Alloy Cluster Complexes. Synthesis and Structural Characterizations of $Pt_4Os_6(CO)_{22}(COD)$ and $Pt_5Os_6(CO)_{21}(COD)_2$

The discovery that platinum alloy clusters have catalytic properties that are far superior to those of pure platinum has led to major improvements in the process of petroleum reforming.[1] This has resulted in an increased interest in the study of the structure, bonding, and reactivity of mixed-metal cluster complexes containing platinum.[2] To date, however, there have been very few reports of high-nuclearity alloy cluster complexes containing platinum.[3-5] We now wish to report the first examples of what may prove to be a series of new high-nuclearity platinum–osmium carbonyl cluster complexes having structures based upon alternating layers of platinum and osmium.

Three products were formed when a hexane solution of $Pt_2Os_3(CO)_{10}(COD)_2$ (**1**)[6] (COD = 1,5-cyclooctadiene) (24.0 mg

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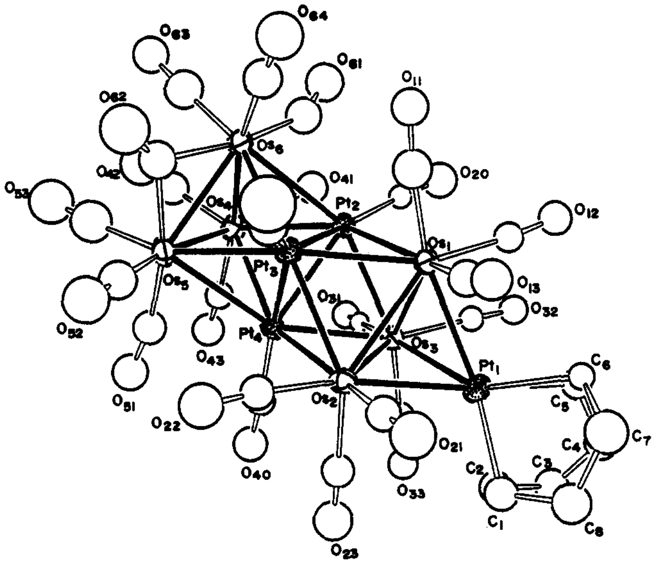

Figure 1. ORTEP diagram of $Pt_4Os_6(CO)_{22}(COD)$ (2), showing 40% probability thermal ellipsoids. Selected interatomic distances (Å, esd = 0.002 Å) are Pt(1)–Os(1) = 2.745, Pt(1)–Os(2) = 2.739, Pt(1)–Os(3) = 2.969, Os(1)–Os(2) = 2.892, Os(1)–Os(3) = 2.987, Os(2)–Os(3) = 3.004, Pt(2)–Pt(3) = 2.636, Pt(2)–Pt(4) = 2.690, Pt(3)–Pt(4) = 2.627, Os(4)–Os(5) = 2.897(2), Os(4)–Os(6) = 2.859, and Os(5)–Os(6) = 2.783.

in 30 mL) was refluxed under nitrogen for 30 min. The products brown **2** (2.1 mg), brown **3** (1.4 mg), and brown **4** (1.1 mg) were separated by TLC on silica gel.[7] Compounds **2** and **4** have been characterized by a combination of IR, ^1H NMR, elemental, and single-crystal X-ray diffraction analyses.[8] Compound **3** is still being characterized. The molecular structure of **2** is shown in Figure 1. The cluster contains three triangular layers of metal atoms stacked face-to-face in staggered conformational arrangements. The inner layer is pure platinum, while the two outer layers are pure osmium. The Pt–Pt distances, 2.627 (2)–2.690 (2) Å, are significantly shorter than the osmium–osmium distances, 2.783 (3)–3.004 (2) Å, but are similar to the Pt–Pt distances found in the series of triangulated platinum clusters $[Pt(CO)_3(\mu\text{-}CO)_3]_n^{2-}$ (n = 2–5) that were prepared and characterized by Chini and Dahl.[9] The staggered stacking of the layers in **2** contrasts with that of the platinum clusters in which the layers were found to lie nearly eclipsed. The platinum atoms in the Pt_3 triangle each contain one linear terminal carbonyl ligand, while each osmium atom contains three. In addition, there is one bridging CO ligand C(62)–O(62) and a Pt(COD) grouping that caps the Os(1), Os(2), Os(3) triangle. The interlayer spacing Os_3–Pt_3 involving the platinum-capped Os_3 triangle, 2.22 Å, is slightly smaller than that involving the uncapped Os_3 triangle, 2.39 Å. The molecule contains a total of 136 valence electrons, which is in accord with Mingos's theory of condensed polyhedra (i.e. two face-shared octahedra with one capping group).[10]

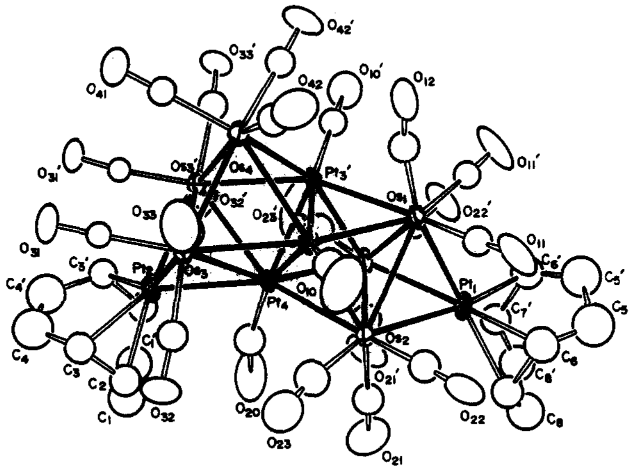

Figure 2. ORTEP diagram of $Pt_5Os_6(CO)_{21}(COD)_2$ (4), showing 40% probability thermal ellipsoids. Selected interatomic distances (Å, esd = 0.002 Å) are Pt(1)–Os(1) = 2.808, Pt(1)–Os(2) = 2.809, Os(1)–Os(2) = 2.949, Os(2)–Os(2′) = 2.923, Pt(2)–Pt(4) = 2.857, Pt(2)–Os(3) = 2.755, Pt(3)–Pt(3′) = 2.635, Pt(3)–Pt(4) = 2.657(2), Os(3)–Os(3′) = 2.796, and Os(3)–Os(4) = 2.846.

The structure of **4** is shown in Figure 2. The molecule contains a crystallographically imposed symmetry plane that passes through the metal atoms Pt(1), Os(1), Pt(4), Os(4), and Pt(2). Its structure is essentially the same as that of **1** except that it contains an additional Pt(COD) capping group Pt(2) that bridges an Os_2Pt triangle between the Pt_3 layer and Os_3 layer Os(3), Os(3′), and Os(4). The Pt_3–Os_3 interlayer spacings in **4** are nearly the same as those in **2**, 2.24 and 2.36 Å, thus indicating that the addition of the capping group Pt(2) does not produce a significant effect on the associated interlayer spacing. Compound **4** contains a total of 148 valence electrons, which is exactly the value expected for a doubly capped cluster of two face-shared octahedra.[10]

The metal nuclearity of **2** can be explained by the combination of two molecules of **1**, but the complete process must also include the addition of two CO ligands. One could imagine the formation of **4** from **2** by the loss of one CO ligand and the addition of a Pt(COD) grouping; however, our attempts to obtain **4** by reaction of **2** with $Pt(COD)_2$ have not yet been successful.

A notable feature of the structures of **2** and **4** is the segregation of the platinum and osmium into alternating layers of the pure elements. It is easy to imagine the extension of this pattern for the formation of larger molecules, and efforts to prepare these are now in progress.

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Supplementary Material Available: For both structural analyses, tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters (23 pages); tables of structure factors (37 pages). Ordering information is given on any current masthead page.

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(7) The yield of **2** is increased slightly to approximately 17% at the expense of **4** (approximately 3%) when **1** is allowed to react with $Pt_2Os_3(CO)_{14}$[6] in a 4:1 ratio in a refluxing solution of hexane for 20 min. Efforts are in progress to try to improve upon the yields of **2–4**.

(8) IR (ν(CO) in CH_2Cl_2; cm^{-1}): for **2**, 2092 (w), 2053 (vs), 2041 (vs), 2021 (w, sh), 1967 (w, br), 1845 (w, vbr); for **3**, 2080 (m), 2044 (vs), 2026 (m), 2016 (w), 1991 (w), 1984 (w); for **4**, 2074 (m), 2041 (s, sh), 2033 (vs), 2023 (s), 1986 (w, br), 1959 (w, br). ^1H NMR (δ in $CDCl_3$): for **2**, 6.00 (t, CH, J_{Pt-H} = 58 Hz), 2.20–2.70 (br, CH_2); for **4**, 5.49 (CH), 5.18 (CH), 2.10–2.75 (Br, CH_2). Anal. Calcd (found) for $2{\cdot}1.5C_6H_6$: Pt, 28.24 (29.19). Calcd (found) for $4{\cdot}C_6H_6$: Pt, 32.54 (30.74), C, 17.22 (15.99), H, 1.01 (0.78). Crystals of **2** and **4** were grown from solutions in a 4:1 CH_2Cl_2/C_6H_6 solvent mixture by slow evaporation of solvent at 25 °C. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromatized Mo Kα radiation. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure-solving program library (version 5.0) obtained from the Molecular Structure Corp., The Woodlands, TX. Crystal data: for **2**, space group = $P2_1/n$, a = 20.404 (6) Å, b = 9.607 (5) Å, c = 24.171 (8) Å, β = 90.512 (3)°, Z = 4, 2847 reflections, R = 0.040; for **4**, space group = $P2_1/m$, a = 12.023 (8) Å, b = 16.010 (9) Å, c = 13.902 (7) Å, β = 103.79 (5)°, Z = 2, 2428 reflections, R = 0.037.

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