of 2,4,6-triisopropylbenzenesulfonyl azide (trisyl azide)[10] for (p-$HO_2CC_6H_4$)SO_2N_3 in the production of compound **4** has shown that the structure of the arylsulfonyl azide apparently is not significant. A slight decrease to 30% yield of **4** after partial purification was observed, which was likely due to the somewhat more difficult chromatographic separation of product **4** from the reaction byproducts.

Studies with *N*-hydroxy β-lactam **9** and trisyl azide illustrated that *only 1 equiv* (100 mol %) of arylsulfonyl azide and *2 equiv* (200 mol %) of base were required for facile conversion into product **10** (eq 3, 62% yield after chromatographic purification with no aqueous workup). However, use of 1 equiv of base (100 mol % of Et_3N) with **9** led to the isolation of intermediate β-lactam **11** (conditions a, Scheme II). β-Lactam **11** could also be obtained by reaction of **9** with trisyl chloride and Et_3N. Furthermore, reaction of **11** with a nucleophilic source of azide effected partial conversion to product **10** (conditions d, Scheme II, ratio of starting material to product was 4 to 5).

On the basis of these results, a plausible mechanism for the azide transfer and N–O bond cleavage of β-lactams **2** and **9** can be proposed (Scheme III). In the presence of base, oxy anion **12** could form (pK_a's of *N*-hydroxy β-lactams similar to **2** and **9** are 6–9)[11] and subsequently attack the arylsulfonyl azide such that azide would be released to yield *N*-arylsulfonyloxy β-lactam **13**. The electron-withdrawing moiety on the β-lactam nitrogen of **13** could facilitate formation of enolate **14**, which might be stabilized as **15** or in enol form **17**. Thus, the negative charge of **14** would be sufficiently distanced from the C_3 position (or be a minor component in equilibrium with **17**) to allow the previously released azide anion to attack, thereby effecting azide transfer *trans* to the pendant C_4 substituent and N–O bond reduction via **15** or **17** in one step. Literature precedent in support of this mechanism was grounded in studies on the solvolysis of α-mesyl or α-triflyl ketones; enolization was determined to be the rate-determining step.[12,13]

Indeed, preliminary studies are consistent with prior sulfonylation followed by azide attack (Scheme III). In fact, it appears that *any* nucleophilic source of azide could be employed to facilitate azide attack on a suitably activated *N*-hydroxy β-lactam. For example, reaction of preformed *N*-tosyloxy β-lactam **19** with trimethylsilyl azide resulted in production of **10** (conditions b and e, Scheme II). Likewise, activation and azide transfer were accomplished just as effectively when diphenylphosphoryl azide[14] was substituted for an arylsulfonyl azide (conditions c, Scheme II).

In summary, diastereoselective azide transfer and N–O bond reduction can be effected by appropriate activation of the *N*-hydroxy moiety of an *N*-hydroxy β-lactam in the presence of base and a nucleophilic source of azide. This remarkable conversion has been accomplished not only sequentially by reaction with an arylsulfonyl chloride and then trimethylsilyl azide (or sodium azide) but also simultaneously with diphenylphosphoryl azide or an arylsulfonyl azide. Diazo transfer can also occur with the latter reagent when the substrate *N*-hydroxy β-lactam structure includes a β-keto ester-containing side chain (Scheme I). Application of these three simultaneous conversions allows the preparation of a fully functionalized β-lactam suitable for elaboration to important carbacephems and related antibiotics.[1,15] *Thus, it appears that substitution of any suitable nucleophile at C_3 may be possible.* Synthetic applicability of the transformation is under current investigation, and additional details are forthcoming.

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Supplementary Material Available: Experimental procedures for the synthesis of all compounds mentioned in the text and tables of X-ray crystallographic data for compound **4** (22 pages); listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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Pure Gold Cluster of 1:9:9:1:9:9:1 Layered Structure: A Novel 39-Metal-Atom Cluster $[(Ph_3P)_{14}Au_{39}Cl_6]Cl_2$ with an Interstitial Gold Atom in a Hexagonal Antiprismatic Cage

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With only a few exceptions (e.g., Mn), nearly all pure metals crystallize in one of the three basic close-packing structures: face-centered cubic (fcc), hexagonal close-packing (hcp), and body-centered cubic (bcc).[1] In the "cluster phase", constraints of the infinite lattice are lifted such that the metal arrangements can adopt any one of the close-packing structures[2–6] or some combination and/or variant thereof (such as pentagonal or icosahedral packing), depending upon the electronic and stereochemical requirements of the metal core and the ligand environment.[7,8] For example, $[Rh_{13}(CO)_{24}H_{5-q}]^{q-2}$ has a 3:7:3 layered hcp structure, whereas $[Pt_{38}(CO)_{44}]^{2-3}$ has a 7:12:12:7 layered fcc structure. $[Rh_{15}(CO)_{27}]^{3-4}$ and $[Rh_{22}(CO)_{37}]^{4-}$,[5] on the other hand, have mixed bcc/hcp and fcc/hcp structures, respectively. We wish to report here a novel pure gold cluster $[(Ph_3P)_{14}Au_{39}Cl_6]^{2+}$ (**1**) which has an unprecedented 1:9:9:1:9:9:1 layered hcp/hcp′ structure (Figure 1a). Cluster **1** represents the largest structurally characterized pure gold cluster known to date.[9]

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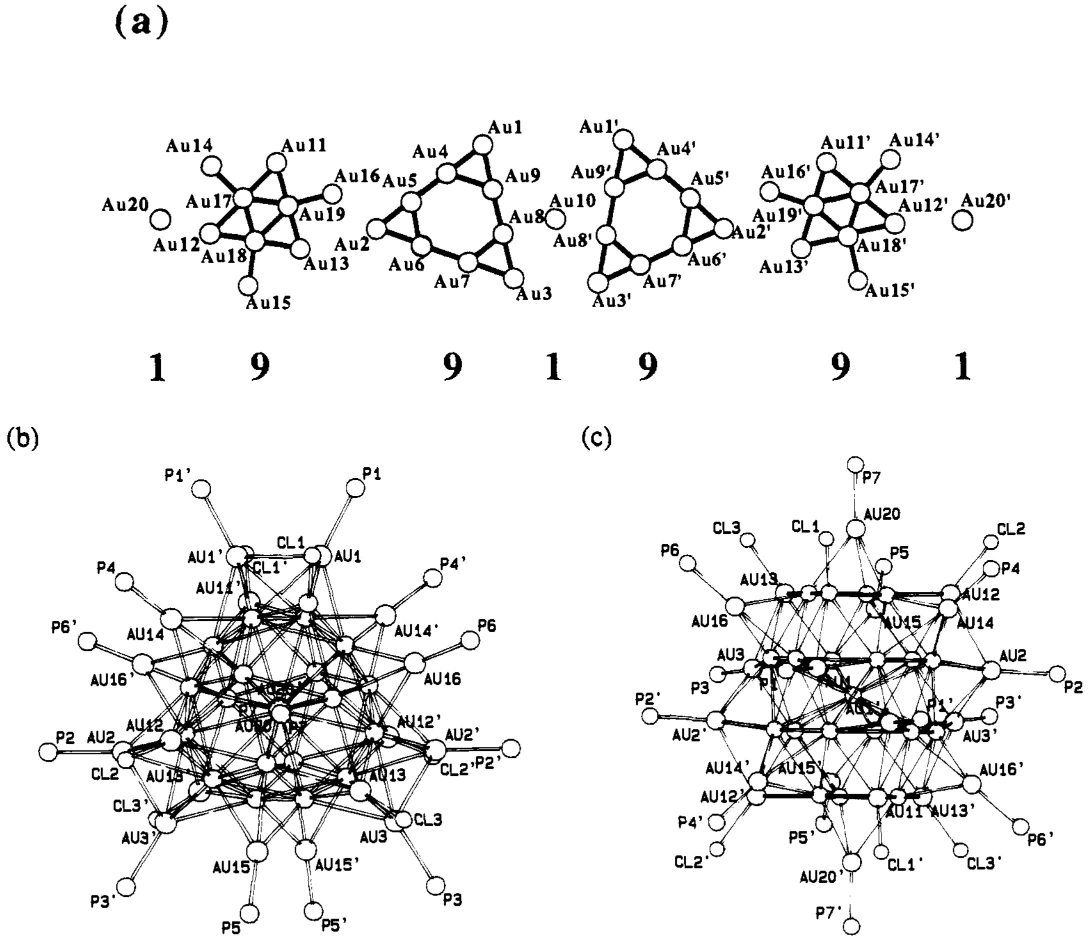
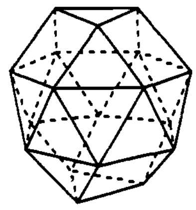


Figure 1. Molecular architecture of the 39-metal-atom cluster $[(Ph_3P)_{14}Au_{39}Cl_6]^{2+}$ (**1**): (a) individual 1:9:9:1:9:9:1 metal layers viewed along the idealized 3-fold symmetry axis; (b) metal–ligand framework, $P_{14}Au_{39}Cl_6$, as viewed along the idealized 3-fold axis; (c) side view of $P_{14}Au_{39}Cl_6$ as projected along the crystallographic 2-fold symmetry axis. The 2-fold symmetry-related atoms are designated as primes. All molecular parameters are normal. The important distances (averaged based on the idealized 3-fold symmetry) are as follows: Au10–Au(4–9), 3.040 (8) Å; Au10–Au(17–19), 3.757 (8) Å; Au4–Au5, 2.792 (8) Å; Au1–Au4, 2.760 (8) Å; Au11–Au17, 2.882 (9) Å; Au17–Au18, 2.734 (8) Å; Au14–Au17, 2.690 (9) Å; Au1–P1, 2.25 (4) Å; Au14–P4, 2.28 (5) Å; Au20–P7, 2.16 (4) Å; Au11–Cl1, 2.33 (4) Å. Typical values of standard deviations of individual distances are given in parentheses.

The title cluster **1** was obtained[10] during an attempt to prepare the pure gold analogue of a series of Au–Ag supraclusters, which have been synthesized and structured by us.[11-17] The metal framework of these latter clusters can be visualized as vertex-sharing polyicosahedra. We refer to these supraclusters as "clusters of clusters" (COC) where the 13-atom icosahedral units serve as basic building blocks. To our surprise, a similar reaction of Ph_3P, $HAuCl_4$, and $NaBH_4$ afforded the pure gold cluster **1**, which may be characterized as a ν_n polytopal cluster built (formally) by a layer-by-layer (LBL) mechanism.[7,8]

Chart I



2

The structure of cluster **1**, which has an idealized $D_3(32)$ point group symmetry, is portrayed in Figure 1.[18] The individual 1:9:9:1:9:9:1 layers of metal atoms, viewed along the idealized

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(10) For preparation and crystallization details, see supplementary material Table G. Though formulated as $[(Ph_3P)_{14}Au_{39}Cl_6]Cl_2$ in this communication, we cannot rule out the possibilities of the presence of hydrides or other ligands in the title compound. A more general formula for **1** should therefore be $[(Ph_3P)_{14}Au_{39}Cl_6H_x]Cl_y$ where $x = 0, 1, 2$ and $y = 1, 2$. Here we assume the presence, if any, of interstitial hydride(s) (probably in the polyhedral cage **2**) only. The value x could go higher if there are surface hydrides.

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(18) The compound $[(Ph_3P)_{14}Au_{39}Cl_6]Cl_2$ forms dark purple-brown prismatic crystals. It crystallizes in the monoclinic space group $C2/c$, $a = 21.897$ (6) Å, $b = 36.915$ (9) Å, $c = 36.636$ (13) Å, $\beta = 92.49$ (4)°, $V = 29585.8$ Å^3, and $Z = 4$. Single-crystal X-ray diffraction data were collected using an Enraf-Nonius diffractometer (Mo Kα radiation). The phenyl groups were refined as rigid bodies with a C(ring)–C(ring) distance of 1.395 Å. Isotropic (heavy atoms)/rigid-body (phenyl groups) refinements gave $R_1 = 7.0\%$ for 2503 independent reflections ($2\Theta \leq 40°$) with $I > 3\sigma$. Anisotropic refinements of the Au atoms did not improve the R values substantially ($R_1 = 6.0\%$). The resulting Au–Au distances did not change by more than 0.01 Å. For crystallographic details, see supplementary material Tables A–F.

3-fold axis (Au10–Au20), are depicted in Figure 1a. The two halves of the molecule are related by a crystallographically imposed 2-fold symmetry axis passing through the central atom (Au10) and the midpoint of Au1 and Au1′. The symmetry-related atoms are designated as primes. Figure 1b,c illustrates the metal–ligand framework. $P_{14}Au_{39}Cl_6$, projected along the idealized 3-fold and the crystallographic 2-fold symmetry axes, respectively.

Referring to Figure 1a and starting from the center (Au10), the first layer A (Au1–Au9) is a ν_3 triangle with the central atom missing, resulting in a tri-edge-capped noncentered hexagon (Au4–Au9). The second layer B (Au11–Au19) is a ν_2 triangle with three vertex caps (Au14–Au16). The inner triangle of this layer (Au17–Au19) is further capped by Au20 in the "third layer" A, giving rise to the 1:9:9:1 layers. The overall 1:9:9:1:9:9:1 layered structure is also portrayed in Figure 1c. In one-half of the molecule, the layered structure 1:9:9:1 can be described as nearly hexagonal close-packing (hcp) A:B:A layering (except that Au10 is displaced toward the center of the cluster). The two halves of the cluster (layers A:B:A and A′:B′:A′) are twisted by 30°, creating a hexagonal antiprismatic hole in which an interstitial gold atom (Au10) resides. This "interface" may be characterized as a "twist dislocation", which is describable as an A:B:A:B:A:B:A hcp arrangement with the central layer (B) missing, followed by a 30° twist of the two halves of the molecule about the idealized 3-fold axis.

The central atom, Au10, which resides at the center of the hexagonal antiprismatic hole, has 12 Au–Au contacts (average distance 3.040 Å) with the two gold hexagons (Au4–Au9 and Au4′–Au9′). The mean Au–Au distance within the hexagons (edge length) is 2.792 Å. The ratio of 3.040/2.792 = 1.089 agrees well with the theoretical value of 1.088. If we include six additional Au–Au distances at an average value of 3.757 Å from layer B (Au17–Au19 and Au17′–Au19′),[19] the central cage can also be described as two half-cuboctahedra fused with a hexagonal antiprism by sharing hexagonal faces (**2**, Chart I). In fact, this 18-vertex polyhedron is one of the 92 possible convex polyhedra with regular faces.[20]

Of the 39 Au atoms, only *one* (the central atom Au10) can be considered as "bulk" atom (completely encapsulated, interstitial atom). The 38 "surface" Au atoms can be categorized into three types: 14 of them are coordinated by phosphine ligands, 6 by terminal chloride ligands, and the remaining 18 are somewhat recessed and *uncoordinated* by ligands. In fact, the 18 unligated Au atoms form the 18-vertex polyhedron **2**. We note that unligated metal atoms on the surface of a cluster are rather unusual and may be important in the understanding of surfaces, interfaces, colloids, catalysts, etc. Including all metal–ligand bonds and Au–Au distances up to 3.12 Å, the coordination numbers for the three types of surface gold atoms under the idealized D_3(32) symmetry are as follows: phosphine-bonded Au1–Au3, 6, Au14–Au16, 4, and Au20, 4; chloride-bonded Au11–Au13, 6; unligated Au4, Au6, and Au8, 10, Au5, Au7, and Au9, 9, and Au17–Au19, 8. As mentioned above, the coordination number of the interstitial gold atom, Au10, is 12.

All bond lengths and angles are normal (see figure caption). The 14 triphenylphosphine ligands coordinate to Au1–Au6, Au20, and their symmetry-related primed atoms with an average Au–P distance of 2.25 Å (the shortest one being Au20–P7 at 2.16 (4) Å). Furthermore, there are only six terminal chloride ligands (attached to Au11–Au13) with an average Au–Cl distance of 2.33 Å.

Attempts to prepare other higher nuclearity pure gold clusters continue.

Acknowledgment. Acknowledgement is made to the National Science Foundation (CHE-9115278) for financial support of this research. We are also grateful to Hy Dang for the drawings of **2** and Figure 1a.

Registry No. **1**·2Cl, 138982-75-9; $HAuCl_4$, 16903-35-8.

Supplementary Material Available: Listings of complete structural data (Table A), positional parameters (Table B), rigid-body group parameters (Table C), interatomic distances (Table D), and interatomic angles (Table E), and details of the preparation and crystallization of $[(Ph_3P)_{14}Au_{39}Cl_6]Cl_2$ (21 pages); tables of observed and calculated structure factors (Table F) (27 pages). Ordering information is given on any current masthead page.

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(19) While a coordination number of 18 is rather unusual in cluster chemistry, some distant analogues can be found in solid-state materials. For example, in $CaCu_5$, the larger Ca atoms are located in a hexagonal ring of Cu atoms which is capped above and below by two additional Cu hexagons, both in staggered configurations, resulting in an 18-coordinated Ca with 6 short Ca–Cu distances of 2.94 Å and 12 long ones at 3.27 Å (Haucke, W. *Z. Anorg. Allg. Chem.* **1940**, 244, 17).

(20) It is commonly known that there are five Platonic (regular) polyhedra, 13 Archimedean (semiregular) polyhedra plus regular prisms and antiprisms, and 92 convex polyhedra with regular faces (but dissimilar arrangements about each of its vertices). For example, see: Coxeter, H. S. M. *Regular Polytopes*; Dover: New York, 1973.

Hydrosilylation–Allylation Sequence for the Stereoselective Elaboration of β-Hydroxy Esters

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The stereocontrolled generation of acyclic 1,3-dioxygenated subunits continues to attract the attention of synthetic organic chemists.[1] β-Hydroxy esters have been found to be particularly valuable as intermediates in this context, as they are widely available in optically and diastereomerically pure forms.[2] However, in order for the ester group to be used to further elaborate the carbon chain, it is generally necessary that it be reduced to the aldehyde oxidation level. Although this may be achieved in principle by a number of hydride reagents,[3] such reductions are often difficult to achieve in practice.[4] Earlier reports from this laboratory described the facile and stereoselective reduction of the carbonyl groups in β-hydroxy ketones via intramolecular hydrosilylation.[5] We now describe an analogous method for the reduction of β-hydroxy esters to the aldehyde oxidation level under remarkably mild conditions and the use of the products in a new method for carbon chain extension occurring with high levels of 1,3-asymmetric induction (Scheme I).

A number of simple β-hydroxy esters were synthesized via the Reformatsky reaction and silylated with Pr^i_2SiHCl/Et_3N/DMAP (cat.) in hexane to give silyloxy esters **1** in yields of 80–90% (Table I). In contrast with our earlier work on β-silyloxy ketones,[5] treatment of **1** with various Lewis acids failed to induce hydride transfer. However, treatment of the silyloxy esters with catalytic amounts of $Bu_4N^+F^-$ in CH_2Cl_2 at 0 °C, in the presence of 4-Å molecular sieves, resulted in clean and nearly quantitative conversions to alkoxysiladioxanes **2** (see Table I).[6] The reactions

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(1) See, for example: (a) Oishi, T.; Nakata, T. *Synthesis* **1990**, 635. (b) Paterson, I.; Mansuri, M. *Tetrahedron* **1985**, *41*, 3569.

(2) For leading references, see: (a) Corey, E. J.; Kim, S. S. *J. Am. Chem. Soc.* **1990**, *112*, 4976. (b) Noyori, R.; Ohkuma, T.; Kitamura, M.; Takaya, H.; Sayo, N.; Kumobayashi, H.; Akutagawa, S. *J. Am. Chem. Soc.* **1987**, *109*, 5856.

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(4) It is noticeable that, despite the availability of direct methods, the reduction of esters to aldehydes is often achieved in practice via a two-step protocol of reduction to the alcohol followed by reoxidation to the aldehyde. See, for example: (a) Heathcock, C. H.; Kiyooka, S.-i.; Blumenkopf, T. A. *J. Org. Chem.* **1984**, *49*, 4214.

(5) (a) Anwar, S.; Davis, A. P. *J. Chem. Soc., Chem. Commun.* **1986**, 831. (b) Anwar, S.; Davis, A. P. *Tetrahedron* **1988**, *44*, 3761. (c) Anwar, S.; Bradley, G.; Davis, A. P. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1383.

(6) For the reduction of esters to alcohols with trialkoxysilanes at elevated temperatures in the presence of cesium fluoride, see: Corriu, R. J. P.; Pertz, R.; Reye, C. *Tetrahedron* **1983**, *39*, 999. For catalysis of the same conversion by an organotitanium species, see: Berk, S. C.; Kreutzer, K. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 5093. The reduction of thiol esters to aldehydes may be accomplished using triethylsilane–10% Pd/C: Fukuyama, T.; Lin, S.-C.; Li, L. *J. Am. Chem. Soc.* **1990**, *112*, 7050.

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