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.

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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

Anthony P. Davis* and Stephen C. Hegarty

Department of Chemistry, Trinity College
Dublin 2, Ireland

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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 $\mathrm{Pr^i{}_2SiHCl/Et_3N}$/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.

[3] (a) Cha, J. S.; Kwon, S. S. *J. Org. Chem.* **1987**, *52*, 5486 and references cited therein. (b) Winterfeld, E. *Synthesis* **1975**, 617.

[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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Scheme I

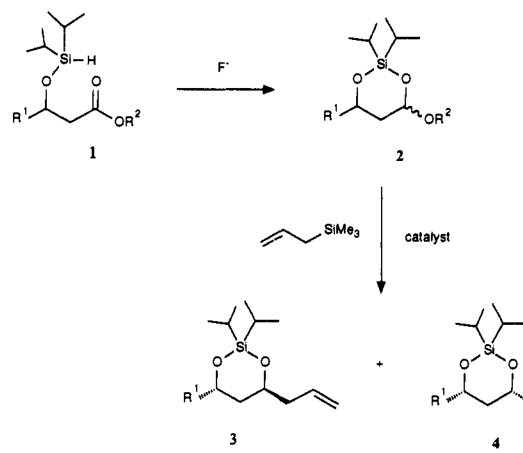


Table I. Synthesis of Alkoxysiladioxanes **2** from *β*-Hydroxy Esters $R^1CHOHCH_2COOR^2$ [a]

R^1	R^2	yield of **1**, %	yield of **2**, % (trans:cis)
Bu	Me	84	98 (1:1)
Pr	Me	83	97 (1:1)
Pr	Me	89	95 (2:1)
Ph	Me	85	96[b] (2:1)
Pr	Et	80	98 (1:1)

[a] The following procedure is typical: To a stirred solution of methyl 3-hydroxyheptanoate (3.52 g, 0.022 mol), triethylamine (2.22 g, 0.022 mol), and 4-(dimethylamino)pyridine (270 mg, 0.0022 mol) in dry hexane (80 mL) under argon was slowly added chlorodiisopropylsilane (3.97 g, 4.1 mL, 0.026) via syringe. The reaction was complete by TLC after 30 min. The mixture was filtered through Celite under reduced pressure. Evaporation of the solvent followed by column chromatography with ether–hexane (1:20) as eluant gave silylated hydroxy ester **1** (R^1 = Bu, R^2 = Me) (5.107 g, 84%) as a colorless liquid. Molecular sieves (4-Å, 100 mg) were activated by heating under vacuum at 200 °C for 2 h. After the flask had cooled, dry dichloromethane (20 mL) and TBAF (58 mg, 0.183 mmol) were added, and the mixture was stirred at room temperature for 15 min before cooling in ice. The silylated hydroxy ester (1 g, 3.67 mmol) was added via syringe. The mixture was stirred at 0 °C for 1 h and then quenched with saturated aqueous sodium hydrogen carbonate. The organic phase was separated and dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. Column chromatography with ether–hexane (1:40) as eluant gave methoxysiladioxane **2** (R^1 = Bu, R^2 = Me) (0.98 g, 98%) as a colorless liquid. [b] Hydrosilylation was performed at −15 °C.

proceeded with low stereoselectivity, in accord with the precedent set by the analogous ketone reductions.[5b] *Remarkably, the conversion of **1** (R^1 = Bu, R^2 = Me) to the corresponding **2** could be performed in 81% yield using ethyl acetate as solvent.* This result provides strong support for our assumption that the hydrosilylation is intramolecular and encourages us to suppose that regioselectivity should be possible in complex substrates containing multiple ester groups.

It seemed that siladioxanes **2** might behave as stereochemically biased equivalents of *β*-hydroxy aldehydes, provided their reactivity could be suitably controlled. In order to examine this possibility, we decided to investigate their reaction with allyltrimethylsilane in the presence of acidic catalysts. We hoped for loss of the alkoxy groups, giving cyclic oxonium ions **5** (which would presumably have a strong preference for the conformation illustrated), followed by allylation to give the diastereomeric siladioxanes **3** and **4** (Scheme I).[7]

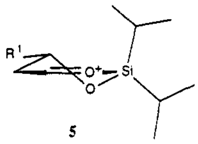
In an initial series of experiments, the alkoxysiladioxane **2** (R^1 = Bu, R^2 = Me) was dissolved in CH_2Cl_2 and treated with allyltrimethylsilane in the presence of a range of acidic catalysts. Many of these reactions resulted in complex mixtures of products but, as shown in Table II, success was met with the silylating agents Me_3SiOTf (Tf = SO_2CF_3) and Me_3SiI, the Lewis acid $SnCl_4$, and the Brønsted superacid $TfOH_2^+B(OTf)_4^-$. The use of the superacid was suggested by our earlier discovery that it may be used to catalyze the addition of allylsilanes to aldehydes.[8,9] It proved to be the most effective by far of the catalysts tried as it was applicable at low concentrations and temperatures to give clean conversions and good stereoselectivities (vide infra). The method was generalized to several other substrates without complications (see Table II).

Table II. Reaction of Alkoxysiladioxanes **2** with Allyltrimethylsilane To Give **3** and **4** (Scheme I)[a]

R^1	R^2	catalyst (mol %)	temp, °C	time, min	yield, %[b]	ratio **6**:**7**[c]
Bu	Me	Me_3SiOTf (10)	25	60	30	7:1
Bu	Me	Me_3SiI (10)	25	60	66	7:1
Bu	Me	$SnCl_4$ (20)	−80	60	83	13:1
Pr	Et	$SnCl_4$ (20)	0	60	84	11:1
Bu	Me	$TfOH_2^+B(OTf)_4^-$ (1–2)	−50	30	85	23:1
Pr	Me	$TfOH_2^+B(OTf)_4^-$ (1–2)	−50	30	81	20:1
Pr	Me	$TfOH_2^+B(OTf)_4^-$ (1–2)	−50	30	80	20:1
Ph	Me	$TfOH_2^+B(OTf)_4^-$ (1–2)	−50	30	78	20:1

[a] All reactions were performed in CH_2Cl_2. Typical procedure for the $TfOH_2^+B(OTf)_4^-$ catalyzed reactions: Allyltrimethylsilane (300 μL, 1.89 mmol) and methoxysiladioxane **2** (R^1 = Bu, R^2 = Me) (500 mg, 1.82 mmol) were stirred in CH_2Cl_2 (25 mL) at −50 °C. $TfOH_2^+B(OTf)_4^-$ (10 μL, 2.5×10^{-2} mmol) was added via syringe. The reaction temperature was maintained at −50 °C for 30 min and then quenched at low temperature with saturated aqueous sodium hydrogen carbonate (10 mL). The organic layer was separated and dried over Na_2SO_4, and the solvent was removed under reduced pressure. Column chromatography with ether–hexane (1:40) as eluant gave allylsiladioxanes **3** and **4** (R^1 = Bu, R^2 = Me) (440 mg, 85%) in the ratio 23:1. The products could be desilylated to give the corresponding diols[12] by treatment with aqueous HF/MeCN.[5] [b] After purification by flash chromatography. [c] Measured by capillary GC.

We were pleased to observe that, as expected, the allylations did show useful levels of stereoselectivity (Table II). The sense of the selectivity, favoring the trans products **3**, is consistent with axial attack by the silane on oxonium ions **5**. Analogies may be drawn with the chelation-controlled attack of nucleophiles via proposed transition states **6**[10,4a] and the axial attack of nucleophiles on 6-membered cyclic oxonium ions **7** (e.g., in C-glycoside synthesis[7c,11]). Indeed, an interesting feature of the present work is that it may be seen as a conceptual link between these two important classes of reactions.



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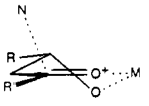

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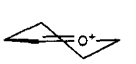

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Acknowledgment. Financial support for this work was provided by the SCIENCE program of the European Community.

Supplementary Material Available: Spectral and analytical data of new compounds and literature references of known compounds (6 pages). Ordering information is given on any current masthead page.

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