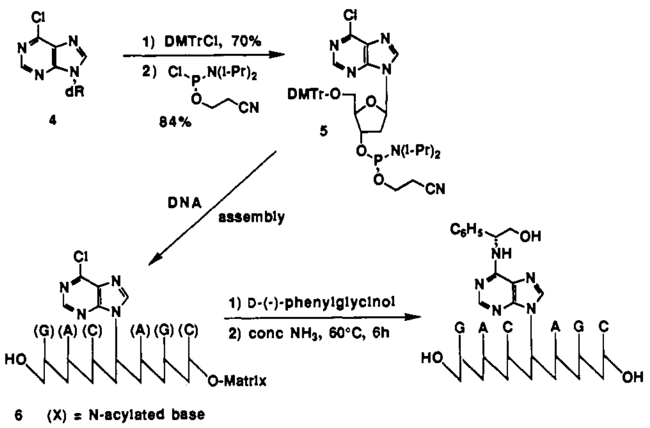
Scheme III



2-Fluorodeoxyinosine (**1**) was used for preparation of the guanine N^2 adduct because the fluorine is more easily displaced than chlorine or bromine.[11] It could be converted to the adducted deoxynucleoside (Scheme I) by treatment with D-(−)-phenylglycinol (3 equiv, DMSO, 5.5 days, 65 °C, 39%). For incorporation into oligonucleotides (Scheme II), nucleoside **1** was converted to 5′-*O*-(dimethoxytrityl) 3′-*O*-phosphoramidite derivative **2**.[12] The target oligonucleotide 5′-CAG-(**1**)-T-3′ was synthesized on a 1.3-μmol scale by the normal automated solid-phase protocol except that **2** was used in twice the normal excess (i.e., 20 equiv) and the reaction time for addition of this nucleoside was extended to 10 min from the usual 1.5. The matrix beads were treated with D-(−)-phenylglycinol (50 mg, 0.050 mL of MeOH, 3 days, 50 °C). The mixture was washed with Et_2O to remove excess phenylglycinol and treated with concentrated NH_4OH (13 h, 60 °C) to remove protective groups. The modified oligomer, 5′-d-(CAG-$G^{2\text{-styr}}$-T)-3′, was purified by SAX ion-exchange chromatography (NH_4OAc/20% EtOH) followed by passage through Sephadex G-15. The structure was confirmed by ^1H NMR; the spectrum was similar to that of unmodified 5′-d(CAGGT)-3′ except for the presence of the phenylglycinol moiety (aromatic protons at δ 7.3–7.4, α-H triplet at δ 5.2). The yield has not yet been fully optimized and is approximately one-third that obtained for *unadducted* oligomer after similar purification. The synthetic method represents an attractive strategy for preparation of oligodeoxynucleotides bearing structurally defined adducts containing reactive functional groups and readily yields the large quantities required for structural studies.

We have extended the method to preparation of N^6 adducts on adenine. Chloro nucleoside **4**[13] was employed as the halonucleoside component. It reacts readily with D-(−)-phenylglycinol to give the adenine N^6 adduct (DMF, 32 °C, 1 day, 59%). 5′-*O*-(Dimethoxytrityl) 3′-*O*-phosphoramidite derivative **5** was prepared uneventfully from **4** and was employed in the synthesis of 5′-d(GAC-$A^{6\text{-styr}}$-AGC)-3′ as shown in Scheme III. The reaction of D-(−)-phenylglycinol with oligomer containing the chloro-substituted adenine precursor was somewhat faster than with oligomer containing 2-fluorodeoxyinosine; the overall yields of the two syntheses were comparable. The synthesis was carried out on a 10-μmol scale. In the NMR spectrum of the oligomer the aromatic protons of the phenylglycinol are at δ 7.3–7.1, and the α-H is at δ 5.31. The structures of the modified oligomers were supported by enzymatic degradation to give the component nucleosides in the expected ratios.[14]

The merits of the halonucleoside strategy for synthesis of styrene oxide adducted oligomers are that it permits assembly with complete regiospecificity of site of adduction in the DNA and with equally complete stereospecificity at the α position of the styrene moiety, since the site of reaction in the oligomer is determined by the placement of the halonucleoside and the configuration of the α position of the styrene moiety is determined by the choice of phenylglycinol enantiomer. Moreover, delaying adduction until after the oligomer has been assembled avoids the need to invoke complex strategies for differential protection and deprotection of the hydroxyl groups in the styrene and deoxyribose moieties during oligomer assembly. We feel that this postoligomerization methodology will be applicable to synthesis of oligomers adducted with a wide variety of mutagens and carcinogens including polycyclic aromatic hydrocarbons where strong economic advantage is provided by late introduction of the costly carcinogen moiety.

Acknowledgment. Generous support of this project by USPHS Grants ES00267 and ES05509 and a fellowship to L.Z. from the Chemical Industry Institute of Toxicology are gratefully acknowledged.

Supplementary Material Available: Structural characterization of new compounds and chromatographic data (8 pages). Ordering information is given on any current masthead page.

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[11] Compound **1** was prepared (75–82%) from O^6-benzyldeoxyguanosine (Kusmierek, J. T.; Folkman, W.; Singer, B. *Chem. Res. Toxicol.* **1989**, *2*, 230–233) by treatment with HF/pyridine and *tert*-butyl nitrite (−25 °C, 10 min) followed by catalytic hydrogenation (5% Pd/C, 3 atm, MeOH, 2 h). The authors cited in ref 7e (which appeared after submission of this manuscript) reported similar synthesis of the O^6-benzyl- and the O^6-(*p*-nitrophenyl)ethyl derivatives of **1** which they employed in reactions with 1-(aminomethyl)pyrene. (a) Montgomery, J. A.; Hewson, K. *J. Am. Chem. Soc.* **1960**, *82*, 463–468. (b) Gerster, J. F.; Robins, R. K. *J. Am. Chem. Soc.* **1965**, *87*, 3752–3759. (c) Gerster, J. F.; Robins, R. K. *J. Org. Chem.* **1966**, *31*, 3258–3262. (d) Robins, M. J.; Uznanski, B. *Can. J. Chem.* **1981**, *59*, 2608–2611.

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Cluster of Clusters. Structure of a Novel Cluster $[(Ph_3P)_{10}Au_{13}Ag_{12}Br_8](SbF_6)$ Containing an Exact Staggered–Eclipsed–Staggered Metal Configuration. Evidence of Icosahedral Units as Building Blocks

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Fivefold symmetry, which is not allowed crystallographically, has been found in quasicrystals.[1] The latter have long-range orientational order but only quasiperiodic translational order. Pentagonal or icosahedral packing (pip) is also quite common in clusters[2] and fine particles[3] where the crystallographical constraints are partially or completely lifted. Pip has also been implicated in the early stages of cluster growth and for structure units in amorphous materials.[4]

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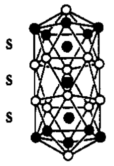
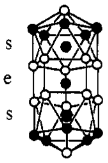
Recently we reported the syntheses and structures of a new series of high-nuclearity Au–Ag clusters[5-10] whose structures are based on vertex-sharing 13-atom centered icosahedra. We refer to these supraclusters as "clusters of clusters".[11,12] The first member of the vertex-sharing icosahedral supraclusters is the 25-metal-atom cluster $[(p\text{-Tol}_3P)_{10}Au_{13}Ag_{12}Br_8]^+$ (**1**),[9] whose metal core can be considered as two Au-centered Au_7Ag_6 icosahedra sharing one vertex (the nuclearity = 2 × 13 − 1 = 25).



1



2

The cluster can also be viewed as having a metal arrangement of 1(Ag):5(Au):1(Au):5(Ag):1(Au):5(Ag):1(Au):5(Au):1(Ag)[13] of D_{5d} symmetry. The four adjacent metal pentagons in **1** are staggered (hereafter designated as s) with respect to one another, giving rise to the staggered–staggered–staggered (sss) configuration. We now report the structure of a novel 25-metal-atom cluster $[(Ph_3P)_{10}Au_{13}Ag_{12}Br_8]^+$ (**2**). Here the two middle pentagons are eclipsed (e), giving rise to a new staggered–eclipsed–staggered (ses) configuration of an idealized D_{5h} symmetry. The observation of both sss and ses configurations for the metal core of the 25-metal-atom clusters **1**[9] and **2** (this work), respectively, can be taken as strong evidence that the basic building block of these clusters is the 13-atom Au-centered icosahedron, which supports the cluster of clusters concept.[11,12]

The title compound (**2**) was prepared by reducing a mixture of Ph_3PAuBr and $(Ph_3P)_2Ag_2Br_2$ (Au:Ag = 1:2) with $NaBH_4$ in absolute ethanol and crystallized from $CH_3CN/EtOH$/hexane. Parts a and b of Figure 1 depict the $Au_{13}Ag_{12}$ core and the $[P_{10}Au_{13}Ag_{12}Br_8]$ framework of **2**. Under $P2_1/m$ space group,[14] the molecule has a crystallographic C_s-m mirror passing through Au13 and the six bridging ligands, Br1–Br6. The 10 triphenylphosphine ligands coordinate to 10 peripheral (surface) Au atoms in a radial fashion. Two terminal ligands, Br11 and Br11′, coordinate to Ag11 and Ag11′, respectively.

The arrangement of the six bridging bromide ligands, connecting the two inner Ag5 pentagons, is rather interesting. Since pentagonal symmetry is incommensurate with the hexagonal net, it is obvious that arrangement of high symmetry is not to be expected. Indeed, as is evident in Figure 1c, there are five doubly bridging (Br1–Br5) and one semiquadruply bridging (Br6) ligands. The latter has two Br6–Ag1 distances of 2.782 (8) Å and two Br6···Ag5 distances of 3.092 (8) Å. Br1 may also be considered as quasi-quadruply bridging as judged by the Br1···Ag2 distance of 3.487 (9) Å. Other important distances can be found in the figure caption.

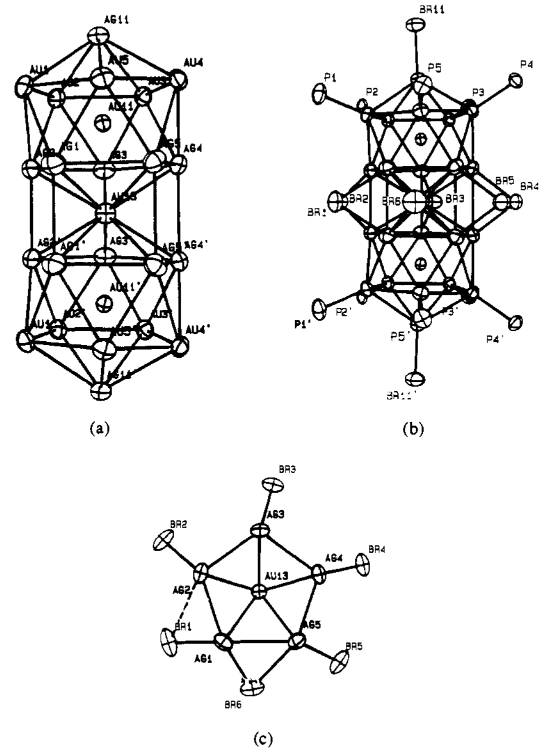


Figure 1. Molecular architecture of the 25-metal-atom cluster $[(Ph_3P)_{10}Au_{13}Ag_{12}Br_8]^+$ as the $(SbF_6)^-$ salt (**2**): (a) the metal core, $Au_{13}Ag_{12}$; (b) the metal–ligand framework, $P_{10}Au_{13}Ag_{12}Br_8$; (c) projection of the two silver pentagons onto the crystallographic mirror (C_s-m) plane passing through the six bridging bromide ligands (Br1–Br6) and Au13. The symmetry-related atoms are designated as primes. The metal core has an idealized 5-fold rotation symmetry (passing through Ag11, Au11, Au13, Au11′, and Ag11′). All radial bonds (12 each) from Au11 and Au11′ have been omitted for clarity. All molecular parameters are normal. The important distances are as follows (Å): Au11–Au(n), 2.718 (av); Au11–Ag(n), 2.826 (av); Au11–Ag11, 2.758 (4); Au11–Au13, 2.845 (2); Au13–Ag(n), 2.892 (av) where n = 1–5; Au–P, 2.30 (av); Ag11–Br11, 2.50 (1); Ag1–Br6, 2.78 (1); Ag1–Br1, 2.68 (1); Ag(2–5)–Br(2–5), 2.58 (av); Ag5···Br6, 3.09 (1); Ag2···Br1, 3.49 (1). The six bridging bromide ligands form a highly distorted hexagon with three sets of nonbonding distances (Å): (1) Br6···Br1, 3.96, and Br6···Br5, 3.80, which are very close to the sum of van der Waals radii (3.90 Å); (2) Br1···Br2, 4.28, and Br5···Br4, 4.22; and (3) Br2···Br3, 5.09, and Br4···Br3, 5.07.

The intraicosahedral metal–metal distances (Au11-centered icosahedra) are significantly shorter than intericosahedral distances (Au13-centered bicapped pentagonal prism), suggesting that intraicosahedral bonding is stronger than intericosahedral bonding, which is consistent with the building-block concept.

Yet another important structural feature of clusters **1** and **2** is that there are three encapsulated metal atoms (Au11, Au11′, and Au13). In **1**, all three are in icosahedral cages. In **2**, Au11 and Au11′ are in icosahedral cages while Au13 resides in a bicapped pentagonal prismatic (bpp) cage. The "centeredness" of such cages is a subject of current interests.[15-22] In fact, *non-*

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[14] Single-crystal X-ray diffraction data were collected by using an Enraf-Nonius diffractometer (Mo radiation). $[(Ph_3P)_{10}Au_{13}Ag_{12}Br_8](SbF_6)\cdot 20EtOH$: monoclinic $P2_1/m$, a = 16.586 (2) Å, b = 24.121 (2) Å, c = 29.969 (3) Å, β = 103.22 (4)°; V = 11 671.8 Å^3, and Z = 2. Anisotropic (heavy atoms)–isotropic (carbon atoms) refinement gave R_1 = 6.3% for 6446 independent reflections ($2\theta \leq 46°$) with $I > 3\sigma$.

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centered icosahedral structure has long been observed in main-group clusters such as $[B_{12}H_{12}]^{2-}$[15] or its analogues[16] and a number of carboranes and metallacarboranes.[17] Transition-metal clusters, on the other hand, can have *centered* icosahedral or bpp cages as exemplified by $[Au_{13}Cl_2(PMe_2Ph)_{10}]^{3+}$[18] and $[Pt_{19}(CO)_{22}]^{4-}$,[19] respectively. Mixed transition-metal/main-group clusters can adopt either *noncentered* (as in $[Ni_{10}(AsMe)_2(CO)_{18}]^{2-}$[20] as well as in metallacarboranes[17]) or *centered* (as in $[Ni_{11}(SnMe)_2(CO)_{18}]^{2-}$[21]) structures. In this respect, clusters **1** and **2** may be considered as the *centered* analogues of the vertex-sharing *noncentered* icosahedral metallacarborane clusters as exemplified by $[M(C_2B_9H_{11})_2]^{n-4}$ where $M^{n+} = Fe^{2+}, Co^{3+}, Ni^{4+}$.[22]

It occurs to us that the ses metal configuration observed in **2** signifies the genesis of a "polyicosahedral" *growth pathway* via vertex sharing to give bi-, tri-, and tetraicosahedral supraclusters as exemplified by the 25-metal-atom (this work), 37-metal-atom $[(p\text{-}Tol_3P)_{12}Au_{18}Ag_{19}Br_{11}]^{2+}$[6] or 38-metal-atom $[(p\text{-}Tol_3P)_{12}Au_{18}Ag_{20}Cl_{14}]$,[7] and 46-metal-atom $[(Ph_3P)_{12}Au_{24}Ag_{22}Cl_{10}]$[8] supraclusters. In all these known structures, the icosahedral units are linked by (interpenetrating) bicapped pentagonal prisms (as in the ses configuration), instead of (interpenetrating) icosahedra (as in the sss configuration).

Acknowledgment is made to the National Science Foundation (CHE-8722339) for financial support of this research.

Supplementary Material Available: Full listings of complete structural data (Table A), positional parameters (Table B), interatomic distances (Table C), interatomic angles (Table D), and anisotropic thermal parameters (Table E) and preparation and crystallization (Table G) for the title compound (26 pages); full listing of observed and calculated structure factors for the title compound (Table F) (69 pages). Ordering information is given on any current masthead page.

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Dicycloproparenes

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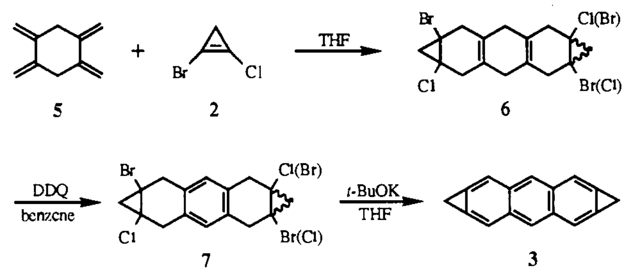
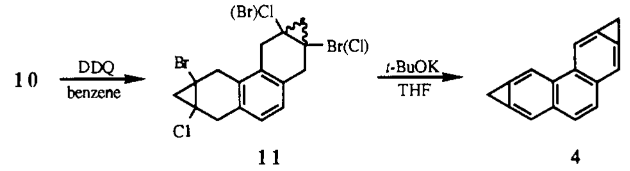
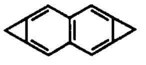
Although benzocyclopropene[2] and its derivatives[3] have become readily available since the report by Anet and Anet[4] describing the synthesis of the first member of this family, the only dicycloproparene that has been reported is the thermally sensitive dicyclopropanaphthalene **1**.[5] We report here the utilization of the cycloproparene synthon 1-bromo-2-chlorocyclopropene (**2**)[6] in the preparation of the novel dicycloproparenes **3**[7] and **4** and some of their derivatives.

Scheme I

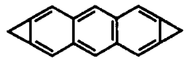


Scheme II

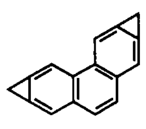




1



3



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The synthetic route to 1*H*,5*H*-dicycloprop[*b*,*i*]anthracene (**3**) is illustrated in Scheme I. Addition of an 8-fold excess of **2**[8] to tetraene **5**[9] in THF at -20 °C for 7 days gave the adduct **6**[10,11] in 80% yield. Treatment of **6** with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in benzene at 50–60 °C for 10 h followed by chromatography afforded **7** in 93% yield. Conversion to **3** was effected by treatment of **7** with potassium *tert*-butoxide in THF at -20 °C for 1 h, providing nearly pure **3** as a fine white solid, mp 127–128 °C dec, in 38% yield after chromatography.

The ^1H NMR spectrum of **3** displays the expected pattern with singlets at δ 3.58 ppm (CH_2), 7.69 (H_2, H_4, H_6, H_8), and 8.45 (H_3, H_7). The ^{13}C NMR spectrum (75.5 MHz) shows signals at δ 18.8 (C_1, C_5), 111.5 (C_2, C_4, C_6, C_8), 123.0 (C_{1a}, C_{4a}, C_{5a}, C_{8a}), 126.8 (C_3, C_7), and 134.8 (C_{2a}, C_{3a}, C_{6a}, C_{7a}). The UV spectrum (pentane) exhibits a maximum at 256 nm (ϵ 35 500) with other absorptions at 332, 348, and 364 nm. The infrared

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(1) American Chemical Society, Division of Organic Chemistry Fellow, 1990–1991, sponsored by the Rohmand Haas Company.

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(8) Billups, W. E.; Lin, L.-J.; Arney, B. E., Jr.; Rodin, W. A.; Casserly, E. W. *Tetrahedron Lett.* **1984**, *25*, 3935.

(9) Longone, D. T.; Boettcher, F.-P. *J. Am. Chem. Soc.* **1963**, *85*, 3436. Longone, D. T.; Warren, C. L. *J. Am. Chem. Soc.* **1962**, *84*, 1507. See also: Bailey, W. J.; Fetter, E. J.; Economy, J. E. *J. Org. Chem.* **1962**, *27*, 3479. Surprisingly, our work represents the first use of **5** in synthesis.

(10) Spectral data and physical constants for new cycloproparenes are as follows. **4**: mp 85–86 °C; ^1H NMR δ 8.64 (d, $J = 1.6$, 2 H), 7.84 (s, 2 H), 7.70 (d, $J = 1.6$, 2 H), 3.59 (s, 4 H); ^{13}C NMR δ 135.0, 134.0, 126.9, 124.8, 123.9, 113.9, 108.3, 19.4; IR 1670 cm^{-1}; UV λ_{max} 250 nm (ϵ 14 500), 282 (8700), 294 (6050), 323 (600); HRMS calcd for $C_{16}H_{10}$ *m/e* 202.0783, found 202.0782. Anal. Calcd: C, 95.02; H, 4.98. Found: C, 94.97; H, 5.05. **12**: pale yellow oil; ^1H NMR δ 7.53 (s, 2 H), 5.55 (s, 2 H), 5.00 (s, 2 H), 3.26 (s, 2 H), 2.63 (s, 4 H); ^{13}C NMR δ 144.5, 136.7, 126.2, 111.2, 108.6, 34.0, 19.2; IR 1655, 1620 cm^{-1}; UV λ_{max} 246 nm (ϵ 5350), 276 (4630), 313 (800); HRMS for $C_{13}H_{12}$ calcd 168.0939, found 168.0942. **13**: mp 125 °C dec; ^1H NMR δ 7.22 (s, 4 H), 4.00 (s, 4 H), 3.29 (s, 4 H); ^{13}C NMR δ 138.9, 124.7, 114.3, 38.0, 20.6; IR 1670 cm^{-1}; UV (pentane) λ_{max} 259 nm (ϵ 1690), 282 (4120), 288 (4010); HRMS calcd for $C_{16}H_{12}$ *m/e* 204.0939, found 204.0941. Anal. Calcd: C, 94.08; H, 5.92. Found: C, 94.14; H, 5.94. **14**: mp 53–54 °C; ^1H NMR δ 7.71 (d, 2 H, $J = 1.5$), 7.20 (d, 2 H, $J = 1.5$), 3.33 (s, 4 H), 2.92 (s, 4 H); ^{13}C NMR δ 139.9, 137.2, 125.4, 125.3, 115.0, 111.5, 30.4, 19.9; IR 1665 cm^{-1}; UV λ_{max} 254 nm (ϵ 1900), 285 (5400), 296 (4700); HRMS calcd for $C_{16}H_{12}$ *m/e* 204.0939, found 204.0938. Anal. Calcd: C, 94.08; H, 5.92. Found: C, 94.05; H, 5.88.

(11) Although the cycloadditions employed to give **6**, **10**, and **16** yield products of unknown stereochemistry, we have not found any evidence that the subsequent reactions are affected by the stereochemistry of the starting material.

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