show a hysteresis of the magnetization curve at 5 K, the nature of which is not understood but which may be due to a Peierls distortion in the borynide chains. This correlates nicely with the observation of additional Bragg reflections in the neutron diffraction pattern at low temperature. To our knowledge, the borynide chain $[B^-]_n$ in LiB_x is the first structurally well characterized linear system which is isoelectronic and isolobal to carbyne.

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A New, Simple Route to Novel Gold Clusters: Structure of an Au_6Ag Wheel with a Gold Rim[**]

Elena Cerrada, María Contel, A. Delia Valencia, Mariano Laguna,* Thomas Gelbrich, and Michael B. Hursthouse

Gold–silver clusters in which the gold and silver atoms can be formally considered in an oxidation state between 0 and 1,[1–7] have attracted considerable attention during the last decade. Apart from such clusters, few complexes containing nonsupported gold–silver bonds, namely $[\{AuAg(C_6F_5)_2L_2\}_n]$,[8, 9] $[Au_2Ag_2(CH_2PPh_3)_4(ClO_4)_4]$,[10] $[\{Au_3(\mu\text{-bzim-}N^3,C^2)_3\}_2Ag]$,[11] and $[Au_4Ag(CH_2SiMe_3)_4(\mu\text{-dppm})_2]CF_3SO_3$[12] have been reported so far (L = tetrahydrothiophene, benzene; bzim = 1-benzylimidazole). For the latter two, the silver center is coordinated solely by gold atoms in a distorted trigonal prismatic and a distorted tetrahedral fashion, respectively.

In this communication, we report on the synthesis of novel heteronuclear compounds containing Au_5Ag and Au_6Ag cores. The X-ray crystal structure of the complex $[Au_6Ag\{\mu\text{-}C_6H_2(CHMe_2)_3\}_6]CF_3SO_3$ confirms the presence of an almost planar $AgAu_6$ core, in which the silver(I) atom is at the center of a regular hexagon of gold atoms. Thus, a "cart wheel"-like arrangement is achieved, in which the six gold–gold interactions form the rim and the six silver–gold bonds the spokes. To the best of our knowledge, this coordination mode for a silver center does not have a precedent in the literature.

Heteronuclear gold–silver compounds (with nonsupported metal–metal bonds) can be obtained by the addition of silver ions to dinuclear[12] or cyclic trinuclear gold(I) complexes.[11]

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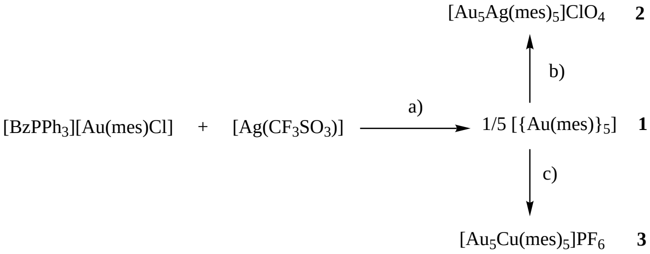
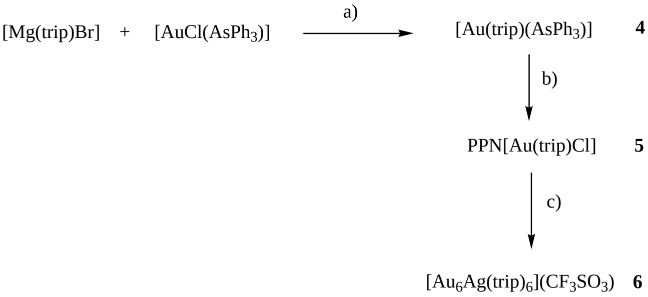
We considered that the addition of metal ions to the pentanuclear gold(I) complex $[\{Au(mes)\}_5]$ (**1**, reported by Floriani et al. in the early 1980s; mes = mesityl = 2,4,6-trimethylphenyl)[13, 14] would be of interest, since such a disposition of gold atoms could potentially donate electron density to another metallic center.

The pentameric starting material was synthesized by us in a simpler way than previously reported—the reaction of $[AuCl(CO)]$[15] with $[\{Ag(mes)\}_4]$[14, 16, 17] requires several steps and special care. The preparation sequence is outlined in Scheme 1 and consists of the reaction of the anionic derivative $(PPh_3Bz)[Au(mes)Cl]$[18] with stoichiometric quantities of $[Ag(CF_3SO_3)]$ in dichloromethane (Bz = benzyl). Precipitation of $(BzPPh_3)(CF_3SO_3)$ and AgCl and subsequent workup of the yellow filtrate gave **1** as a solid in a moderate yield. Subsequent reaction of **1** with $AgClO_4$ (Scheme 1 b) gave a solution from which $[Au_5Ag(mes)_5]ClO_4$ (**2**) precipitated as a green solid. The reaction of **1** with $[Cu(CH_3CN)_4]PF_6$ afforded $[Au_5Cu(mes)_5]PF_6$ (**3**) as a red solid.



Scheme 1. Synthesis of $[\{Au(mes)\}_5]$ (**1**) and subsquent gold–silver- and gold–copper complexes **2** and **3**. a) – AgCl, – $(BzPPh_3)(CF_3SO_3)$ (molar ratio 1:1); b) $AgClO_4$ (molar ratio 1:1); c) $[Cu(NCCH_3)_4]PF_6$ (molar ratio 1:1).

Mass spectrometry (LSIMS$^+$, nitrobenzylalcohol matrix) of complexes **2** and **3** showed the parent ion $[Au_5M(mes)_5]^+$ (M = Ag, Cu) as the base peaks of *m*/*z* values of 1687 (100 %) and 1643 (100 %), respectively, with loss of the anions. The remaining peaks are associated with the pentanuclear species $[Au_4M(mes)_4]^+$ at *m*/*z* (%) 1371 (89) and 1327 (54), tetranuclear $[Au_3M(mes)_3]^+$ at 1055 (24) and 1011 (21), trinuclear $[Au_2M(mes)_2]^+$ at 739 (39) and 695 (40), and dinuclear $[AuM(mes)]^+$ at 423 (44) and 379 (37) for **2** and **3**, respectively. The ^{1}H NMR spectrum of **2** showed three resonances of equivalent mesityl groups, from *m*-H, *o*-CH_3, and *p*-CH_3, that are shifted downfield compared to the spectrum of **1**. It is worth noting that, because the two *m*-H and the *o*-CH_3 protons are inequivalent, the ^{1}H NMR spectrum of **3** has five resonances. The spectrum of **2** at $-60\,^{\circ}C$ showed a broadening of the resonances of the *m*-H and *o*-Me protons rather than a split into two signals, as found for **3**.



Scheme 2. Synthesis of complexes **4**–**6**. a) 0 °C (molar ratio 1.5:1); b) PPN^+Cl^- (molar ratio 1:1); c) $[Ag(CF_3SO_3)]$ (molar ratio 1:1 or 1.25:1).

Unfortunately, it was not possible to obtain crystals suitable for an X-ray diffraction study from **2** and **3**. Hence, we have carried out the analogous reactions (Scheme 2) with an alternative gold(I) precursor in which the mesityl group is replaced by the bulkier tris(isopropyl)phenyl ligand (trip, 2,4,6-$[(CH_3)_2CH]_3C_6H_2$). Starting from Br(trip), we reacted BrMg(trip) with $[AuCl(AsPh_3)]$ to provide $[Au(trip)(AsPh_3)]$ (**4**) which, when treated with PPN^+Cl^-, afforded PPN-[Au(trip)Cl] (**5**; PPN = bis(triphenylphosphine)iminium). The reaction of **5** with equimolecular quantities of $[Ag(CF_3SO_3)]$ did not afford the homoleptic trip derivative similar to **1** but the heterometallic green complex $[Au_6Ag(trip)_6]CF_3SO_3$ (**6**) instead. Complex **6** could be obtained in better yield if the reaction was carried out in the presence of a small excess (1–1.25:1) of $[Ag(CF_3SO_3)]$. In contrast to the previously described complex $[\{Au_3(\mu\text{-bzim-}N^3,C^2)_3\}_2Ag]$[11], **6** was not found to be luminescent.

The mass spectrum (LSIMS$^+$) of **6** showed the parent ion $[Au_6Ag(trip)_6]^+$ at *m*/*z* (%) 2507 (10) and loss of the $CF_3SO_3^-$ ion. The ^{1}H NMR spectrum of **6** showed eight signals of the equivalent tris(isopropyl)phenyl groups assigned to two *m*-H singlets, three *o*- and *p*-CH septets, and three doublets from the CH_3 moieties. Clearly, the tris(isopropyl)phenyl units do not rotate within the NMR time scale. This behavior is similar to what was observed (for the mesityl groups) in the ^{1}H NMR spectrum of **3** and in the low temperature spectrum of **2** (see above).

The molecular structure of the cation of compound **6** · ½ CH_2Cl_2 is shown in Figure 1. It is based upon a ring of six gold atoms with the silver atom at its center. Each Au position deviates slightly (by 0.028 Å) but systematically (alternating above/below) from the least-square plane calculated for the entire Au_6Ag unit. As imposed by crystallographic symmetry, Ag is located exactly on this plane. The gold–silver atomic distances within this novel Au_6Ag core are 2.797(1), 2.802(1), and 2.809(1) Å, which can be considered as formal gold–silver bonds.[11, 12] The gold–gold distances range over 2.795(1)–2.817(1) Å and are slightly longer than those observed for the pentamer **1** (2.697(1)–2.708(1) Å).[13, 14] Furthermore, the C_{ipso} atoms of the tris(isopropylphenyl) groups serve as bridges between two consecutive gold atoms within the hexagon. With values between 2.111(7) and 2.200(7) Å, the Au–C distances are similar to those in other aryl-bridged complexes[13, 18, 19] or in seminal aromatic derivatives.[20] As observed for the previously mentioned mesityl complexes, the planar tris(isopropylphenyl) groups are nearly perpendicular to the mean plane through the gold and silver atoms, so that the angle between the average planes of Au_6Ag and the C11–C16 ring is 85.7°. However, the planes of the phenyl rings are slightly bent towards one of the adjacent gold atoms, for example, the angle Au1-C11-C14 is 125.5° but Au2-C11-C14 is 153.6°. Moreover, the six C_{ipso} atoms around the Au_6 hexagon

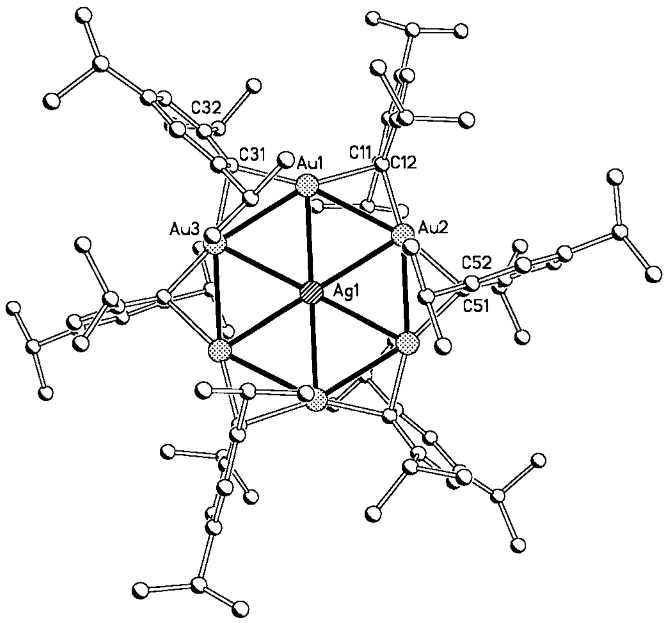


Figure 1. The structure of the cation of complex **6** in the crystal. Atomic radii are arbitrary and H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ag1-Au1 2.8022(9), Ag1-Au2 2.797(1), Ag1-Au3 2.809(1), Au1-Au2 2.795(1), Au1-Au3 2.798(1); Au1-Ag1-Au2 59.97(3), Au3-Ag1-Au1 60.21(3), Au2-Ag1-Au3 60.05(3).

deviate from the Au_6Ag plane by 0.75 Å, three lie above and three below the plane.

The ^1H NMR spectrum of complex **6**, as discussed above, is in accordance with its structure being maintained in solution. Thus, complexes **2** and **3** should present similar structures with five gold – mesityl fragments (indicated by their mass spectra).

In conclusion, the reaction sequence to generate **1** (Scheme 1 a) shows a general method to synthesize $[(AuR)_n]$ complexes, which could be extended to other radical and/or metallic centers. In addition, the preparation of **6** is a rare example of template synthesis for a hexaatomic gold rim. We are currently researching reactions with different organic ligands and the effects of addition of different metallic ions to these $[AuR]_n$ species.

Experimental Section

1: To a solution of $(PPh_3Bz)[Au(mes)Cl]$[18] (0.5 mmol) in dichloromethane (40 mL), a solution of $[Ag(CF_3SO_3)]$ (0.5 mmol) in diethyl ether (10 mL) is added. Precipitated AgCl was removed through celite filtration. The solution was concentrated to about 2 mL and addition of diethyl ether (30 mL) precipitated $(BzPPh_3)(CF_3SO_3)$, which was also removed by filtration. Concentration of the solution to about 5 mL and addition of *n*-hexane (30 mL) afforded **1** as a pure solid (yield: 49 %).

2 and **3**: To a diethyl ether solutions of **1** (0.25 mmol) 0.05 mmol of $AgClO_4$ [or $[Cu(CH_3CN)_4]PF_6$] were added at 0 °C. Concentration of the deep green [deep red] solution to about 5 mL and addition of *n*-hexane (20 mL) precipitated **2** (yield: 40 %) [**3** (yield: 50 %)] as a green [red] solid.

Compounds **4** and **5** were obtained in 80 and 90 %, respectively. The reactions are similar to those previously reported for their mesityl analogues.[18]

6: To a solution of **5** (0.25 mmol) in dichloromethane (30 mL), $[Ag(CF_3SO_3)]$ (0.042 mmol) was added. Preciptated AgCl was filtered. Addition of of diethyl ether (30 mL) precipitated $PPN(CF_3SO_3)$ which was also separated by filtration. Concentration of the solution to about 5 mL and addition of *n*-hexane (20 mL) afforded **6** as a deep green solid (40 %).

Microcrystalline samples of complexes **1** – **6** gave satisfactory elemental analyses. Selected NMR data at room temperature (^1H NMR: 300 MHz, $CDCl_3$, $SiMe_4$; $^{31}P\{^1H\}$ NMR: 121 MHz, $CDCl_3$, external 85 % H_3PO_4). **1**: ^1H: $\delta = 6.75$ (s, 2 H; *m*-H), 2.62 (s, 6 H; *o*-CH_3), 2.14 (s, 3 H; *p*-CH_3). **2**: ^1H: $\delta = 6.84$ (s, 2 H; *m*-H), 2.76 (s, 6 H; *o*-CH_3), 2.14 (s, 3 H; *p*-CH_3). **3**: ^1H: $\delta =$ 6.88 (s, 1 H; *m*-H), 6.86 (s, 1 H; *m*-H), 2.67 (s, 3 H; *o*-CH_3), 2.63 (s, 3 H; *o*-CH_3), 2.14 (s, 3 H; *p*-CH_3). **4**: ^1H: $\delta = 7.59 – 7.4$ (m, 15 H), 6.97 (s, 2 H), 3.6 (sept, 2 H, $^2J_{H,H} = 6.9$ Hz; *o*-$CH(CH_3)_2$), 3.6 (sept, 1 H, $^2J_{H,H} = 6.9$ Hz; *p*-$CH(CH_3)_2$), 1.35 (d, 12 H; CH_3), 1.23 (d, 6 H; CH_3). **5**: ^1H: $\delta = 7.64 – 7.21$ (m, 60 H; PPN), 6.76 (s, 2 H), 3.81 (sept, 2 H, $^2J_{H,H} = 6.9$ Hz; *o*-$CH(CH_3)_2$), 2.74 (sept, 1 H, $^2J_{H,H} = 6.9$ Hz; *p*-$CH(CH_3)_2$), 1.16 (d, 18 H; CH_3); $^{31}P\{^1H\}$: $\delta =$ 21.7 (s; PPN). **6**: ^1H: $\delta = 7.08$ (s, 1 H), 6.78 (s, 1 H), 3.91 (sept, 1 H, $^2J_{H,H} =$ 6.8 Hz; $CH(CH_3)_2$), 3.08 (sept, 1 H, $^2J_{H,H} = 6.8$ Hz; $CH(CH_3)_2$), 2.74 (sept, 1 H, $^2J_{H,H} = 6.8$ Hz; $CH(CH_3)_2$), 1.64 (d, 6 H; CH_3), 1.09 (d, 6 H; CH_3), 0.56 (d, 6 H; CH_3).

Crystal data for **6** $\cdot \frac{1}{2} CH_2Cl_2$: $C_{92}H_{140}AgAu_6Cl_2F_3O_3S$, $M_r = 2743.67$, triclinic, space group $P\bar{1}$, $a = 13.532(3)$, $b = 13.973(3)$, $c = 14.240(3)$ Å, $\alpha = 90.93(3)$, $\beta = 105.4(3)$, $\gamma = 95.89(3)^\circ$, $V = 2579.5(3)$ Å^3, $Z = 1$, $\mu = 8.802$ mm^{-1}, $F(000) = 1314$, $T = 150$ K. 32159 reflections were collected in an Enraf – Nonius Kappa CCD diffractometer, of which 9109 were independent ($R_{int} = 0.060$). Correction were made with the SORTAV program.[21] 33 distance restraints were applied to refine the positions of two disordered isopropyl groups. Hydrogen atoms were placed in calculated positions. The final $wR(F^2)$ was 0.106 for 9109 data, 488 parameters, with a conventional $R(F)[F^2 > 2\sigma(F^2)] = 0.041$. Max./min. electron density = 1.806/ – 3.400 e Å^3. Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-141781 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Photoregulation of the DNA Polymerase Reaction by Oligonucleotides Bearing an Azobenzene**

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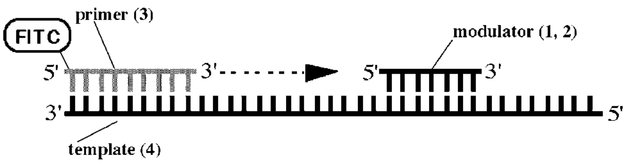
Regulation of bioreactions by external stimuli has been one of the most attractive and urgent themes of recent research.[1] The activities of enzymes have been photomodulated by attaching azobenzene and spiropyran near to their active centers.[2, 3] Furthermore, growth and differentiation of cells have been controlled by applying electric voltage.[4] However, little has been known about artificial control of biosynthesis of DNA. Here we report the first photoregulation of a template-dependent DNA polymerase reaction. By using photoresponsive oligonucleotides as modulators and irradiating with appropriate light, DNA of predetermined length is selectively produced from one template DNA.

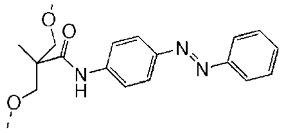
The oligonucleotides used here are presented in Figure 1. The modulator **1b** bears an azobenzene for photoinduced *cis–trans* isomerization.[5] Its 3′ terminus is protected by a 3-hydroxypropyl residue to avoid DNA elongation from that point. The primer DNA **3** (18-mer) is labeled with fluorescein isothiocyanate (FITC) at the 5′ end. The template DNA **4** is a 54-mer. When DNA polymerization with T7 DNA polymerase was achieved at pH 7.5 and 34 °C in the dark in the presence of **1b**, only 34-mer DNA was produced (lane 3 in Figure 2). Apparently, the DNA elongation was blocked by **1b**, and stopped at its 5′ terminus. Under irradiation with UV light ($300 < \lambda < 400$ nm), however, the 34-mer DNA was not formed and instead 54-mer DNA was predominantly produced (lane 4, Figure 2). Depending on whether the light is used or not, either of these two DNAs is selectively obtained from one template.[6] The irradiation causes no significant effects on the enzymatic activity, as confirmed by careful control experiments. When unmodified oligonucleotide (**1a**) was used as the modulator, only the 34-mer DNA was produced either in the dark or under UV irradiation (lanes 1 and 2, Figure 2).



modulators
1a: 5'-GGGGAATTCGGA-3'-C$_3$-spacer
1b: 5'-GXGGAATTCGGA-3'-C$_3$-spacer
2a: 5'-GGGGAATTCGGATTTTTTTT-3'
2b: 5'-GXGGAATTCGGATTTTTTTT-3'

primer
3: (FITC)-5'-CTAATACGACTCACTATA-3'

template
4: 3'-GATTATGCTGAGTGATATAAAAAAAAA-
-AAAAAAACCCCTTAAGCCTAAAAAAAA-5'

X =


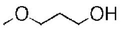
C$_3$-spacer =


Figure 1. Strategy for the photoregulation of a T7 DNA polymerase reaction. In the modulators, **X** denotes the residue carrying an azobenzene.

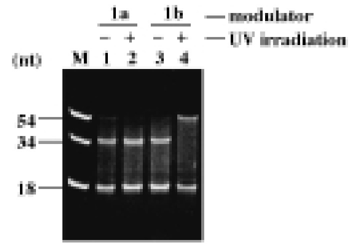


Figure 2. Polyacrylamide gel electrophoresis patterns for the T7 DNA polymerase reactions at pH 7.5 and 34 °C for 20 min. Lane 1: with the unmodified oligonucleotide **1a** in the dark; lane 2: with **1a** under UV irradiation; lane 3: with the modified oligonucleotide **1b** in the dark; lane 4: with **1b** under UV irradiation; lane M: markers (18-mer, 34-mer, and 54-mer).

Before the UV irradiation, the azobenzene in **1b** mostly takes the *trans* form.[5] Here, the melting temperature (T_m) of the duplex between **1b** and **4** is 57 °C (measured at 260 nm under the reaction conditions), and this duplex is almost completely formed at the reaction temperature (34 °C). The *trans*-azobenzene has a planar structure, and is favorably accommodated in the duplex. When the T7 DNA polymerase moves along the template **4** in the $3' \rightarrow 5'$ direction during the polymerization, it cannot go through this double-stranded region (This enzyme requires single-stranded DNA as template) and the DNA elongation terminates at the 5′ end of **1b**. Under UV irradiation, the azobenzene in **1b** is isomerized to the *cis* form. This isomer is nonplanar so that its steric repulsion against **4** weakens the binding of **1b** to **4**. This effect

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