Formation of novel anionic gold–tin cluster compounds

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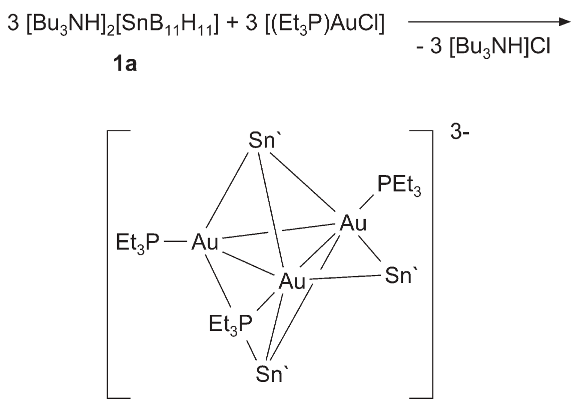
A straightforward procedure for the formation of mixed metal Au/Sn clusters is presented: reaction of the heteroborate $[SnB_{11}H_{11}]^{2-}$ with phosphine gold electrophiles gave the clusters $[Bu_3NH]_3[\{(Et_3P)Au(SnB_{11}H_{11})\}_3]$ and $[Bu_3MeN]_4$-$[\{(dppm)Au_2(SnB_{11}H_{11})_2\}_2]$, which were characterised by X-ray diffraction.

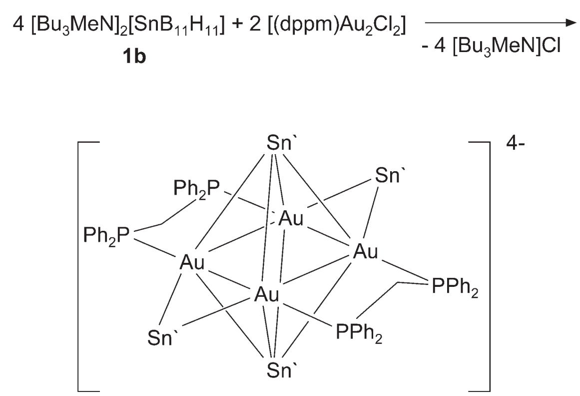
The syntheses, chemistry, and physical properties of homoatomic gold clusters have been a subject of continuing interest in recent years.[1,2] Furthermore a wide variety of high co-ordinated main-group element-centered gold clusters have been published.[3] Besides many other synthetic procedures, aggregation of gold atoms can be achieved, for example, by reduction of gold(I) complexes, photolysis of $[(Ph_3P)AuN_3]$ or transfer of a LAu-fragment from $[LAu]_3O^+$ to the respective main group element.[4–6] We are investigating the co-ordination abilities of the heteroborate stanna-*closo*-dodecaborate $[SnB_{11}H_{11}]^{2-}$ which is accessible in amounts of around five grams following a two step procedure invented by Todd *et al.* in 1992.[7] Recently we found that in reaction with the gold electrophile $[(Ph_3P)AuCl]$ formation of a Au/Sn cluster $[\{(Ph_3P)Au(SnB_{11}H_{11})\}_2]^{2-}$ occurs and the tin nucleophile exhibits in solution as well as in the solid state for the first time a bridging coordination mode.[8] In order to investigate a possible stereochemical influence on the tin–gold cluster formation reaction we started to vary the phosphine coligand. Thus, we report here on the reaction of the tin borate **1** with $[(Et_3P)AuCl]$ (Scheme 1) and $[(dppm)Au_2Cl_2]$[9] (Scheme 2) in CH_2Cl_2. A trinuclear gold cluster **2** was isolated in 71% yield from the 1 : 1 reaction of the dianion **1** and $[(Et_3P)AuCl]$.[10] The salt **2** was characterized by NMR spectroscopy and crystal structure analyses. In the ^{11}B NMR spectrum two signals at −6.8 and −14.2 ppm with an intensity ratio of 1 : 10 indicate substitution at the tin vertex of the heteroborate. ^{31}P NMR spectra were recorded at room temperature and 193 K: one signal in the room temperature spectrum at 50.8 ppm with tin satellites (^2J $^{119/117}Sn$–^{31}P = 232.8 Hz) exhibiting intensities equivalent for coupling with three tin atoms is a good indicator for the formation of the trianion $[\{(Et_3P)Au(SnB_{11}H_{11})\}_3]^{3-}$ showing dynamic behavior in solution. At 193 K, in accordance with the solid state structure, an AB_2 system was detected in the ^{31}P NMR spectrum: the signal at 51.2 ppm (P1,2) exhibits tin satellites with the μ_2 (286.7 Hz) and μ_3 (55.2 Hz) bridging cluster ligands whereas the resonance at 52.6 ppm (P3) shows satellites (311.6 Hz) only with the triply bridging clusters. Single crystals suitable for X-ray structure analyses were obtained from CH_2Cl_2–hexane by slow diffusion. **2** crystallizes with one equivalent of dichloromethane in the triclinic space group $P\bar{1}$.[10] The geometry of the metal core in the anion of **2** (Fig. 1) shows a surprising correspondence with the respective In–Au arrangements in $[(dppe)_2Au_3In_3Cl_6(thf)_3]$ and $[(dppe)_2Au][(dppe)_2Au_3In_3Br_7(thf)]$.[11] In **2** the atoms P1–Au1–Au2–P2 show an arrangement close to linearity. This edge of the Au_3-triangle is μ_2 bridged by a tin ligand and exhibits the shortest Au–Au distance with 260.6(1) pm, whereas the other two Au–Au distances are much longer [289.4(1), 279.3(1) pm]. This bonding situation and the interatomic distances can be compared with the Au_2Sn_2 and Au_2Sn_3 core in the clusters $[\{(Ph_3P)Au(SnB_{11}H_{11})\}_2]^{2-}$ and $[(Ph_3P)_2Au_2(SnB_{11}H_{11})_3]^{4-}$.[8]



$[Bu_3NH]_3[\{(Et_3P)Au(SnB_{11}H_{11})\}_3]$

2

Scheme 1 Synthesis of the trinuclear gold cluster **2**. Sn′ = $[SnB_{11}H_{11}]^{2-}$.



$[Bu_3MeN]_4[\{(dppm)Au_2(SnB_{11}H_{11})_2\}_2]$

3

Scheme 2 Synthesis of a tetranuclear gold complex **3**. Sn′ = $[SnB_{11}H_{11}]^{2-}$, [dppm = bis(diphenylphosphino)methane].

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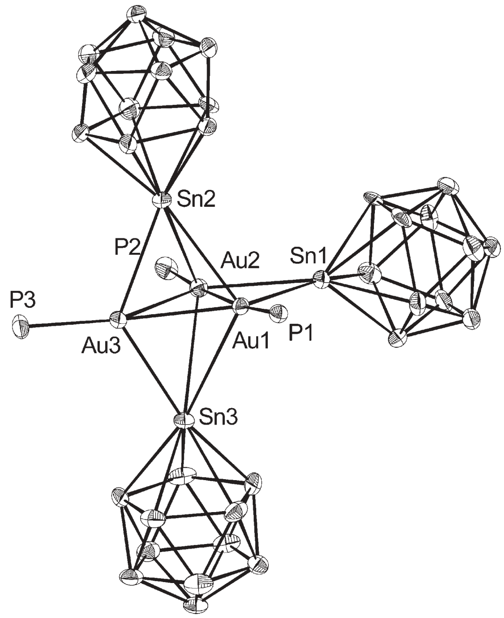

Fig. 1 Molecular structure of the anion of **2**. Ethyl substituents at phosphorus have been omitted for reasons of clarity.

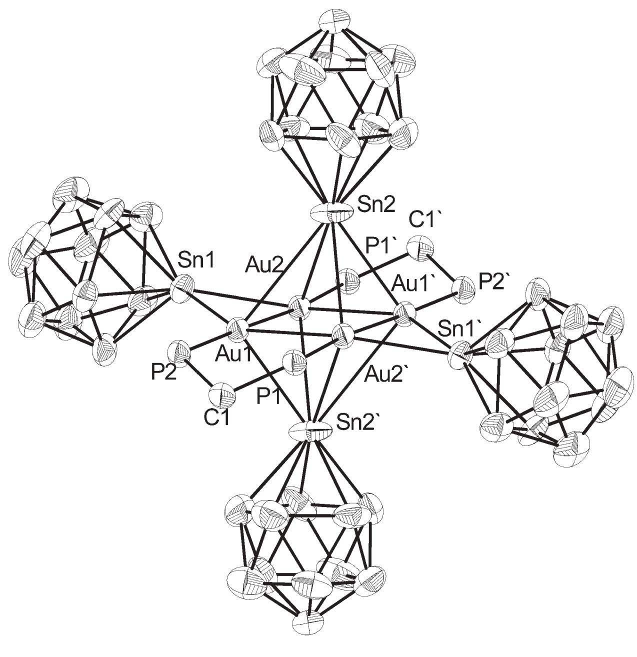

Fig. 2 Molecular structure of the anion of **3**. Phenyl substituents at phosphorus have been omitted for reasons of clarity.

From the reaction with the dinuclear gold electrophile [(dppm)Au_2Cl_2] (Scheme 2) a tetranuclear cluster **3** was isolated and identified by X-ray structure and elemental analyses.[12] Due to low solubility of $[Bu_3MeN]_4[\{(dppm)Au_2(SnB_{11}H_{11})_2\}_2]$ it is impossible to detect any NMR signals in solution. However crystals were grown from CH_2Cl_2 and the geometry of the anion of **3** is shown in Fig. 2. The tetraanion lies on a center of symmetry and shows a rectangle for the four gold atoms. Bridged by the heteroborate the Au1–Au2 edge is much shorter [262.17(4) pm] than the chelated unit Au1–Au2′ [284.75(5) pm]. The borate clusters coordinate in two different modes on the Au_4-rectangle: the known μ_2-bridging mode and a μ_4-co-ordination with three shorter interatomic distances [Sn2–Au2 312.41(8), Sn2–Au1′ 283.98(8), Sn2–Au2′ 301.64(6) pm] and one relatively long contact [Sn2–Au1 330.41(8) pm]. Interestingly, the geometry of the heavy atoms Sn and Au in **3** is closely related to the arrangement of the copper and iodine atoms in $[\{(dppm)Cu_2I_2\}_2]$.[13] So far complexes with Au–Sn contacts are rare and a tin ligand for systematic gold cluster formation is not known.[14]

In conclusion, the heteroborate $[SnB_{11}H_{11}]^{2-}$ is a new ligand for gold cluster formation. Bridging an Au–Au edge a short interatomic distance around 260 pm results.

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10 A sample of **1a** (124.3 mg, 0.20 mmol) was added to a dichloromethane solution (20 mL) of [$(Et_3P)AuCl$] (70.1 mg, 0.20 mmol) at room temperature. After stirring for 1 h the solvent was removed and the mixture was washed with water. The remaining solid was dried under vacuum and yellow crystals of **2** (106.5 mg, 71%) were obtained by slow diffusion of hexane into a dichloromethane solution of the reaction product. Anal. Calcd. for $C_{54}H_{162}Au_3B_{33}N_3P_3Sn_3$ (2250.6): 28.82 C, 7.26 H, 1.87 N, found: 28.65 C, 8.08 H, 2.04 N. ^{11}B NMR (64 MHz, CD_2Cl_2) δ −14.2 (B2–B11), −6.8 (B12). ^{31}P {^1H} NMR (202 MHz, CD_2Cl_2, 293 K) δ 50.8 (s, ^2J $^{119/117}Sn–^{31}P$ = 232.8 Hz); (193 K) δ 51.2 (s, ^2J {$^{119/117}Sn–^{31}P$ = 55.2 Hz; $^{119/117}Sn–^{31}P$ = 286.7 Hz}), 52.6 (s, ^2J {$^{119/117}Sn–^{31}P$ = 311.6 Hz}). X-ray crystal structure analysis of **2**: crystal data for $C_{54}H_{162}Au_3B_{33}N_3P_3Sn_3 \cdot CH_2Cl_2$, M = 2335.40, triclinic, space group $P\bar{1}$ (No. 2), a = 1568.5(1), b = 1671.4(1), c = 2181.3(2) pm, α = 100.47(1), β = 97.73(1), γ = 116.27(1)°, V = 4.8901(7) nm^3, ρ_{calc} = 1.586 g cm^{-3}, μ = 5.375 mm^{-1}, Z = 2, λ = 71.073 pm, T = 120 K, 61516 reflections collected, 18924 independent (R_{int} = 0.097) and 11114 observed reflections [$I > 2\sigma(I)$], 923 refined parameters, R_1 = 0.041, wR_2 = 0.080, all data R_1 = 0.085, wR_2 = 0.089. CCDC 253768. See http://www.rsc.org/suppdata/cc/b4/b416472e/ for crystallographic data in .cif or other electronic format.

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12 A sample of **1b** (129.9 mg, 0.20 mmol) was added to a dichloromethane solution (20 mL) of [(dppm)Au_2Cl_2] (84.9 mg, 0.10 mmol) at room temperature. After stirring for 1 h the solvent was removed and the mixture was washed with water. The remaining solid was dried under vacuum and yellow crystals of **3** (131 mg, 39%) were obtained by slow diffusion of hexane into a dichloromethane solution of the reaction product. Anal. Calcd. for $C_{102}H_{208}Au_4B_{44}N_4P_4Sn_4$ (3353.1): 36.54 C, 6.25 H, 1.67 N, found: 36.15 C, 6.23 H, 1.52 N. Crystal data for $C_{102}H_{208}Au_4B_{44}N_4P_4Sn_4$, M = 3352.87, triclinic, space group $P\bar{1}$ (No. 2), a = 1559.3(1), b = 1558.9(1), c = 1748.4(2) pm, α = 68.08(1), β = 64.03(1), γ = 74.25(1)°, V = 3.5147(5) nm^3, ρ_{calc} = 1.584 g cm^{-3}, μ = 4.944 mm^{-1}, Z = 1, λ = 71.073 pm, T = 160 K, 54953 reflections collected, 15436 independent (R_{int} = 0.067) and 9957 observed reflections [$I > 2\sigma(I)$], 593 refined parameters, R_1 = 0.044, wR_2 = 0.098, all data R_1 = 0.075, wR_2 = 0.106. CCDC 253769. See http://www.rsc.org/suppdata/cc/b4/b416472e/ for crystallographic data in .cif or other electronic format.

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