

Synthesis of a Tri(gold)boride Complex (Cy₃P)B[AuP(*o*-Tol)₃]₃

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A tri(gold)boride of the formula B[AuP(*o*-Tol)₃]₃ (**2**) is generated in the reaction of the silylated phosphine borane Cy₃PBH₂SiMe₃ with the tri(gold)oxonium tetrafluoroborate [(*o*-Tol)₃PAu]₃O⁺BF₄⁻ and isolated as its stable 1 : 1 complex with tricyclohexylphosphine: Cy₃PB[AuP(*o*-Tol)₃]₃. The composition of the product has been confirmed by elemental analyses and mass spectrometry. Solution NMR data of **2** indicate a molecular structure with C_{3v} symmetry which has been confirmed by MP2 calculations for the model system H₃PB(AuPH₃)₃. The compound is a rare case of a trimetallated boride which is isolobal with the simple phosphineborane Cy₃PBH₃. With reagents bearing less bulky substituents (R₃ = ^tPr₃, MePh₂, Ph₃), the reactions proceed to salts with the tetra-aurated cations [Cy₃PB(AuPR₃)₄]⁺.

Key words: Gold, Boride, Phosphine Borane, Boron Coordination

Introduction

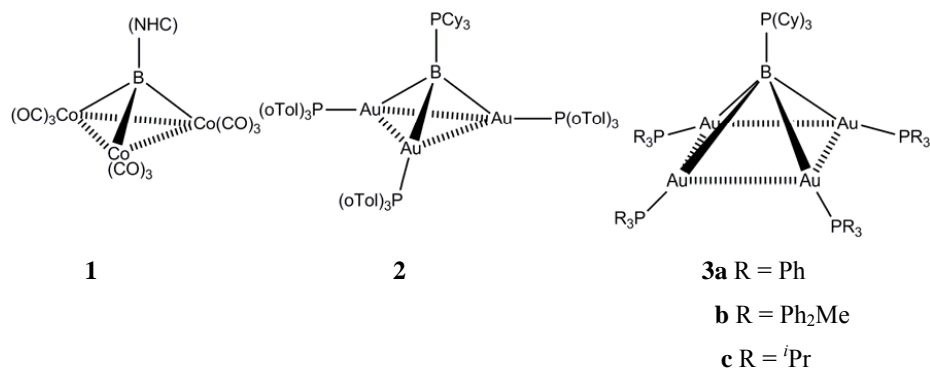
There is currently a growing interest in boron compounds with a boride character, *i. e.* with negatively polarized or negatively charged boron atoms. As summarized in a recent publication [1], within only a short period there have been various successful synthetic approaches to generate compounds with boride centers in various coordination environments [2–4]. Reflecting the general movement in ligand chemistry from tertiary phosphines to carbenes, most of the newly designed systems are based on the latter, which proved to be more variable and more efficient in stabilizing boride functions.

In another very recent publication a tris(tricarbonyl-cobalt)boride complex stabilized by a *N*-heterocyclic carbene ligand (NHC = 1,3-dimesityl-imidazol-2-ylidene) has been presented as an unprecedented trinuclear μ₃-boride compound (**1**, Scheme 1) [5]. The synthesis followed a straightforward 1 : 3 metathesis reaction of the complex (NHC)BBr₃ with three equivalents of sodium tetracarbonylcobaltate. The core unit features a tetracoordinate boron atom with the carbene

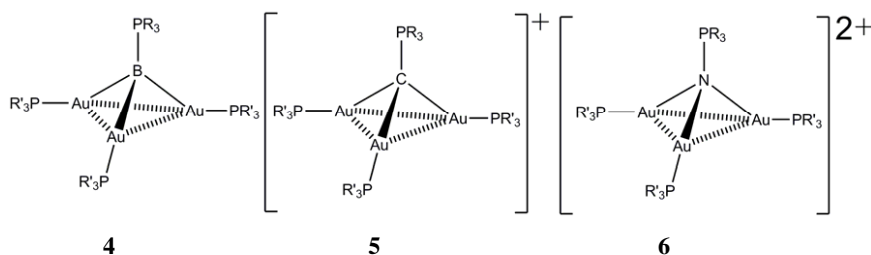
carbon atom in an apical position and the cobalt atoms at the trigonal base.

This communication has prompted us to report on details of an earlier synthesis of the title trinuclear gold compound (**2**, Scheme 1) which have never been fully disclosed. Composition and a proposed structure were shown in review articles [6, 7], but the full account has subsequently not been published because the structural characterization was incomplete owing to failures of all attempts to grow single crystals.

In order to point out that there is an alternative synthesis available for trinuclear μ³ boride compounds, and to provide some spectroscopic data for reference, we describe here our preparative concept and its results for the special combination of substituents shown in **2**. The formation of the tetra-aurated cation **3a** (Scheme 1) obtained with another set of phosphines has been presented in an early communication [8]. This work has been extended as shown here. The present communication is also an addition to the discussion of the isolobality concept [9] which relates [LAu]⁺ cations with the proton H⁺ (L = donor ligand), and thus the title compound with the simple phosphine borane Cy₃PBH₃.



Scheme 1.



Scheme 2.

Concept and Results

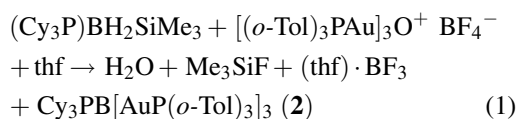
Following successful studies of the poly-auration of carbon, nitrogen, phosphorus, arsenic, oxygen, sulfur, selenium, tellurium, chlorine, and bromine [10–12] our group had become interested in compounds with poly-aurated boron atoms [8]. Theoretical investigations had shown that a boron-centered hexagold cluster trication $[B(AuL)_6]^{3+}$ should be a stable species (L = tertiary phosphine) [13, 14], and that compounds with lower degrees of auration and a mixed substitution pattern might also become available on the way to complete auration. This idea of the existence of molecules of the type **4** (a more general formula for **2**) was the more attractive since isoelectronic tri-aurated triarylposphonium ylide cations (**5**) and triarylposphonium imide dications (**6**) had also been shown to be readily accessible, and that their tetrafluoroborates are surprisingly stable (Scheme 2) [15–17].

After several unsuccessful attempts with various sorts of starting materials, the silylated phosphine borane $Cy_3PBH_2SiMe_3$ was chosen [18, 19] in which the polarity of the unique bond $B^{\delta-}-Si^{\delta+}$ may provide some boride character for electrophilic substitu-

tion at the boron atom with aurating agents $[LAu]^+$. A related process had also been helpful to convert the silylated ylide $Ph_3P=CHSiMe_3$ with its protic hydrogen atom ($=CH-$) into compounds **5**. Owing to the strongly reduced hydridic character of hydrogen atoms in phosphine boranes [20], the $-BH_2-$ group in $Cy_3PBH_2SiMe_3$ could finally allow complete auration. The favorable 3 : 3 stoichiometric relation of suitable functions in $Cy_3PBH_2SiMe_3$ on the one hand, and in reagents of the type $[(LAu)_3O]^+$ on the other hand, appeared to offer the right conditions for the envisaged metathesis. It should be noted that similar effects have now been demonstrated for carbene-boranes [1].

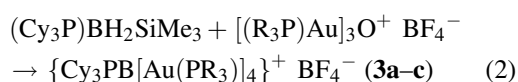
The first experiments showed, however, that the reaction proceeded beyond the tri-auration (**2**) to give tetra-aurated cations of the type of compound **3a** [8]. This tendency towards poly-auration was not unprecedented, as similar reactivity has been discovered in the auration of carbon centers [10–12]. In that chemistry it could also be demonstrated that steric bulk of the substituents can prevent poly-auration simply owing to lack of space at the carbon center [21]. For that reason, in the work described herein, a tri(gold)oxonium salt with tri(*o*-tolyl)phosphine ligands was chosen.

Carried out in tetrahydrofuran, the reaction follows at least in part the stoichiometry shown in Eq. 1:



The product can be precipitated as a pale-yellow microcrystalline powder from the filtrate of the reaction mixture by addition of pentane in *ca.* 35% yield based on the oxonium salt. The compound is air stable for short periods, soluble in tetrahydrofuran, dichloromethane and chloroform, but poorly soluble in diethyl ether, benzene and pentanes. It decomposes upon heating above 145 °C. Using an excess of (Cy₃P)BH₂SiMe₃ (up to a molar ratio of 1 : 3) does not lead to a different product. The consecutive poly-auration steps are obviously faster than the mono-auration step, which is due to the steady increase of favorable aurophilic interactions in the products [10–12]. The very moderate yield is probably due to secondary reactions of the by-products which include water and the BF₃ solvate. Most of these by-products become insoluble and are separated in the filtration of the reaction mixture.

With the tri(gold)oxonium salt [O(AuPCy₃)₃]⁺BF₄[−], fully protected also with the very bulky Cy₃P ligands, no reaction was observed with (Cy₃P)BH₂SiMe₃. By contrast, introduction of tri(*iso*-propyl)phosphine or dimethyl(phenyl)phosphine as ligands at the gold atoms gave the corresponding tetra-aurated cations **3** with Me₂PhP (**3b**) or ^{*i*}Pr₃P (**3c**). The Eq. 2 for this reaction is difficult to balance because the products are formed in moderate yields irrespective of the molar ratio of the reactants employed. The driving force of the tetra-auration is again the clustering of the gold atoms:



The square-pyramidal structure of the cations contained in **3** has been determined for the phenylated case (**3a**, R = Ph) [8].

The composition of the title compound **2** has been confirmed by elemental analysis and mass spectrometry. FAB-MS (from 4-nitrobenzyl alcohol) gave the molecular ion [M]⁺ at *m/z* = 1796.0 (12.5% relative intensity), followed by the fragments *m/z* = 1491.6

(9.1), 1295.5 (12.9), 805.2 (56.7), and 781.3 (100) for [M–P(*o*-Tol)₃]⁺, [M–AuP(*o*-Tol)₃]⁺, [AuP(*o*-Tol)₃]₂⁺, and [(Cy₃P)AuP(*o*-Tol)₃]⁺, respectively.

The ¹H and {¹H}¹³C NMR spectra of **2** (in CDCl₃ at 25 °C) show the expected sets of resonances (Experimental Section). The {¹H}³¹P and {¹H}¹¹B spectra (also in CDCl₃, 25 °C) contain two broad signals with δ(P) = 38.3 [3P, P(*o*-Tol)₃] and 40.5 ppm [1P, PCy₃], and a single broad resonance at δ(B) = –20.5 ppm, respectively. These spectra confirm the presence of the two sorts of PR₃ units, the equivalence of the three [P(*o*-Tol)₃] ligands, and the absence of BF₄[−] anions. Some complementary analytical and spectroscopic data for **3b**, **c** are given in the Experimental Section (for **3a**, see ref. [8]). The broadening of the ¹¹B and ³¹P signals is not surprising since the former and ¹⁹⁷Au are quadrupolar nuclei (*s* = 3/2) and the symmetry of the molecule (**2**) or the cations (**3**) is low.

The calculated structure of the model system H₃PB[Au(PH₃)]₃

Because all attempts to grow single crystals of **2** have failed, the structure of a model system with hydrogen atoms instead of Cy or *o*-Tol groups as substituents to all four phosphorus atoms (**4**, R = H) was calculated by MP2 methods. The results are shown in Fig. 1. In its ground state the molecule has C₃ symmetry with the B and P atoms in slightly distorted tetrahedral and the gold atoms in linear coordination geome-

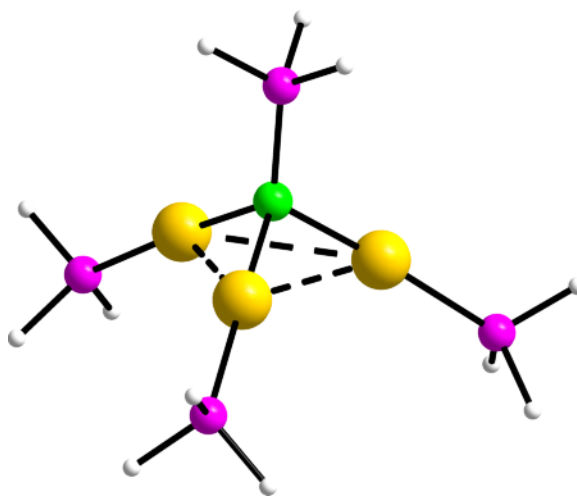


Fig. 1. Calculated structure of the model compound H₃PB(AuPH₃)₃ (**4**, R = H).

Table 1. Selected bond lengths (Å), bond angles and dihedral angles (deg) in the calculated model compound **4** (R = H).

Atoms	Distance	Atoms	Angle
Au–B	2.040	B–Au–P	176.67
Au–P	2.275	P–B–Au	119.31
P–B	1.839	Au–B–Au	98.09
		H–P–B–Au	60.0
		H–P(Au)B–P'	0.0

try. The conformation at the B–P unit is staggered, and the three AuPH₃ tetrahedra are eclipsed relative to the boron tetrahedron. No other ground states were found using various different starting structures, all of which led to the same ground state except for an all-staggered structure, which was found to be a transition state of third order.

The calculations yielded a set of bond lengths and angles (Table 1) which are in good agreement with experimental data for related molecules. The edges of the equilateral Au₃ triangle are 3.082 Å long and thus in the range which suggests significant aurophilic interactions [10–12]. The B–Au–P axes deviate very little from linearity (176.67°), but the direction of the bending indicates Au...Au attraction. Accordingly, the Au–B–Au angles are smaller than the tetrahedral standard (98.08°) while the P–B–Au angles are larger (119.31°). The Au–B distance in **4** (R = H) is 2.040 Å, and thus shorter than the range of 2.16(1)–2.19(1) Å observed in **3a** (R = Ph) with its pentacoordinated B atom. The P–B distance is 1.839 Å, which probably for the same reason is also shorter than the P–B distance in **3a** of 1.92(1) Å, but similar to the data found in standard phosphine-boranes with tetracoordinate B atoms [20]. Owing to the C_{3v} symmetry, the dihedral angle H–P–B–Au of 60.0° indicates a perfectly staggered conformation, and the dihedral angle H–P–(Au)–B–P shows that there is no distortion away from an eclipsed conformation of the units under consideration.

Summary

The results described herein have shown that phosphineboride trianions [R₃PB]³⁻ can function as μ₃ capping units for a triple of ligand-protected gold cations [R'₃PAu]⁺. The resulting molecules R₃PB(AuPR'₃)₃ (**4**) are isoelectronic analogs of the cationic species [R₃PC(AuPR'₃)₃]⁺ (**5**) and

[R₃PN(AuPR'₃)₃]²⁺ (**6**) described earlier [15–18]. Taking the proton [H]⁺ as isolobal with the cation [R'₃PAu]⁺, the relation to simple phosphine-boranes R₃PBH₃ is also obvious [9].

With examples now being known for such diverse elements as *cobalt* and *gold*, there is good reason to assume that many more cases with similar structure and bonding characteristics will be accessible. For future endeavors it will be useful to know that preparative attempts need not only rely on metathesis reactions of (L)BX₃ complexes of boron halides, like (R₃P)BX₃, with alkali metallates, but can also employ silylated boranes, like R₃PBH₂SiMe₃, which are also readily accessible and easy to handle.

Experimental Section

All experiments were carried out in an atmosphere of dry and pure nitrogen. Glassware was oven-dried and filled with nitrogen. Solvents were dried and purified using established methods. Cy₃BH₂SiMe₃ was prepared following a procedure published previously [19]. Tri(gold)oxonium salts were also obtained according to syntheses described in the literature: R₃P = Ph₃P [22], Cy₃P [23], (*o*-Tol)₃P [24], ⁱPr₃P [25], MePh₂P [26].

NMR instruments: Jeol GX 270 and GX 400; δ(¹H) and δ(¹³C) values are referenced to TMS (calculated from the residual solvent signal), δ(³¹P) and δ(¹¹B) to external 85% aqueous phosphoric acid and external trimethylborate, respectively. Mass spectrometer: Finnigan MAT 311 with fast atom bombardment (FAB). Photoluminescence: Perkin Elmer LS50B, 25 °C. Elemental analyses: TU München in-house combustion (C, H) and AAS instruments (Au).

Synthesis of compound **2**

A solution of Cy₃BH₂SiMe₃ (420 mg, 1.15 mmol) in 10 mL tetrahydrofuran is added slowly at 25 °C to a suspension of {[*o*-Tol)₃PAu]₃O}⁺ BF₄⁻ (520 mg, 0.32 mmol) in 20 mL tetrahydrofuran. The reaction mixture is stirred in a closed vessel for 4 d and filtered. Pentane is added to the filtrate to induce precipitation of the product, which is separated by filtration and dried in a vacuum. Yield 201 mg (35%, relative to the oxonium component), yellowish microcrystalline powder, dec. 167 °C. – Elemental analysis: C₈₁H₉₆Au₃BP₄ (1795.86): calcd. C 54.17, H 5.39, Au 33.09%; found C 53.98, H 5.30, Au 33.67%. – NMR (CDCl₃, 25 °C): δ(H) = 1.0–2.2 (m, 33H, Cy), 6.9–7.4 (m, 54H, C₆H₄), 2.3 (s, 9H, Me); δ(C) = 128.2 (d, ¹J_{P,C} = 44.1 Hz, C1), 142.6 (d, ²J_{P,C} = 11.0 Hz, C2), 126.6 (s, C3), 131.0 (s, C4), 131.9 (s, C5), 133.7 (s, C6), 23.1 (s, Me) for *o*-Tol; 37.0 (d, ¹J_{P,C} = 34.5 Hz, C1'), 25.8 (s, C'2,6), 27.8 (s, C'3,5), 25.4 (s, C'4) for Cy.

Synthesis of **3b**

A solution of Cy₃BH₂SiMe₃ (800 mg, 2.19 mmol) in 10 mL of tetrahydrofuran is added to a stirred suspension of [(MePh₂P)Au]₃O⁺ BF₄⁻ (450 mg, 0.24 mmol) in 20 mL of the same solvent. After stirring in a closed vessel for 1 d the reaction mixture is filtered. The brown filtrate is concentrated in a vacuum and the product precipitated with diethyl ether. Yield 212 mg (47 %, relative to the oxonium component), pale-brown microcrystalline solid, dec. 174 °C. – NMR (CDCl₃, 25 °C): δ(P) = 22.1 (br, 3H, PPh₂Me), 25.8 (br, 1H, PCy₃); δ(B) = 14.0 (br, PBAu₃), –1.6 (s, BF₄⁻). – MS ((+)-FAB): *m/z* (%) = 1880.0 (17) [M]⁺, 678.3 (19.3) [Cy₃PAuPPh₂Me]⁺, 598.1 (57.5) [Au(PPh₂Me)₂]⁺, 397.6 (100) [Au(PPh₂Me)]⁺.

Synthesis of **3c**

The same procedure with 250 mg (0.68 mmol) Cy₃BH₂SiMe₃ and 360 mg (0.31 mmol) [(ⁱPr₃P)Au]₃O⁺ BF₄⁻ gives a yellow-brown microcrystalline product; yield 224 mg (40 %, relative to the oxonium component), dec. 138 °C. – NMR (CDCl₃, 25 °C): δ(P) = 75.6 (b, 3P, PⁱPr₃), 18.4 (b, 1P, PCy₃); δ(B) = 20.1 (b, PBAu₄), –1.6 (s, BF₄⁻).

– MS ((+)-FAB): *m/z* (%) = 637.7 (21) [(Cy₃P)Au(PⁱPr₃)]⁺, 517.5 (56) [Au(PⁱPr₃)₂]⁺, 357.3 (100) [Au(PⁱPr₃)]⁺.

Calculation of the molecular structure of H₃PB(AuPH₃)₃ (**4**, R = H)

The structures of the model compound were preoptimized with the *ab initio* hybrid density functional B3LYP method in GAUSSIAN09 [27, 28] and then optimized on the MP2 level of theory [29]. The def2-TZVP basis sets and an additional ECP for Au were applied in the calculations [30]. All structures were fully optimized, and the optimized structures were confirmed as true local minima by performing harmonic frequency calculations. PH₃ groups were rotated in relaxed energy scans to locate other minima on the PES, however none were found.

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