

Regular article

Structure and stability of gold-substituted diborane, boranes, and borohydride ions

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Abstract. Pseudopotential ab initio calculations were performed for species of the type $\text{BH}_n(\text{AuPH}_3)_m^k$, where $n + m = 3$ or 4 , and the charge k is $-2, \dots, +1$. Some derivatives of these and diaurated diboranes were also studied. The structural data agree well with the available experimental evidence. Factors affecting the stability of these systems, including the role of aurophilic attraction, are discussed. The singly charged anions and the diaurated diboranes are predicted to be the most stable members of these series.

Key words: Gold – Boron – Closed-shell attraction – Pseudopotentials – Second-order Møller–Plesset perturbation theory

1 Introduction

Centered gold clusters of the type $\text{X}(\text{AuL})_n^{m+}$, where the central atom is carbon, nitrogen, oxygen, or their analogs from the rows further down the periodic system, are well known experimentally and have recently been studied theoretically [1–3]. The role of strong closed-shell gold–gold attraction [4] (sometimes called “aurophilic attraction”) in their stability and, in many cases, structure is well established. The aurophilic attraction can be defined as an attraction between two closed-shell, nominally Au(I) subsystems. There are no valence electrons that could be attributed to this $\text{Au} \cdots \text{Au}$ bond. Its strength can approach that of the weakest covalent bonds [4]. The experimental evidence can be structural, energetic, or Raman.

Analogous systems where the central atom is boron are, however, almost unknown. The only experimentally

known species of this type is $(\text{Cy}_3\text{P})\text{B}[\text{Au}(\text{PPh}_3)]_4^+$, where Cy means cyclohexyl and Ph is phenyl [5]. Theoretical calculations exist for BAu_n ($n = 4, 5, 6$) [6], $\text{B}(\text{AuPH}_3)_n$ ($n = 4, 5$) [2], and $\text{B}(\text{AuPH}_3)_6$ [1]. None of these calculations were carried out with the basis sets and correlation methods considered necessary today for an accurate description of the closed-shell gold–gold attractions [7].

The phosphinegold group (Au-PH_3) and its substituted analogs are isolobal with the hydrogen atom [8]. Although the hydrogen and gold s orbital energies and radii are quite different, their chemical behavior can be analogous. In diatomic AuH, the atoms are nearly neutral [9], thus, these boron-centered systems are analogous with borane (BH_3) and borohydride ions (BH_3^+ , BH_4^- , BH_3^{2-}). In practice, however, boron forms the diborane molecule B_2H_6 instead of BH_3 ; therefore one can expect that a gold-substituted diborane may be experimentally accessible as well.

The aim of the current study is to computationally map out the boron-centered gold clusters of the type $\text{X}(\text{AuL})_n^q$, $n = 1, \dots, 4$, $q = -2, \dots, +1$, as well as the di(phosphinegold)-substituted diboranes, $\text{B}_2\text{H}_4(\text{AuPH}_3)_2$, in order to estimate the feasibility of their possible synthesis, and to predict the structures.

2 Method

The technical requirements for a feasible description of the systems of this type, including the gold–gold attraction, have been studied previously [7] and were adhered to without modifications. The Stuttgart relativistic effective core potentials and the corresponding basis sets [10, 11] were employed for all atoms except hydrogen. The latter were modeled with the Huzinaga $2s/4s$ basis [12]. Where applicable, the basis sets were decontracted for split-valence quality. Polarization functions were added to all atoms. The details are provided in Table 1.

The geometries were optimized at the second-order Møller–Plesset (MP2) level, employing the resolution of identity (RI-MP2) [13–15] approach. The auxiliary basis sets required for the description of electron densities at this approximation were generated as uncontracted even-tempered ones with an exponent ratio of 3.0. The auxiliary basis sets are documented in Table 2. At optimized geometries, single-point energies were calculated at the regular MP2 level.

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Hartree–Fock-level (HF) geometry optimizations were also performed. Since van-der-Waals-type interactions are essentially absent in calculations performed at this level, the role of the gold–gold attraction in determining the structures can thus be studied. Our previous studies [3, 7, 16, 17] have shown that the MP2 approach overestimates the attraction; thus, the experimental geometrical parameters influenced by it are expected to be bracketed between HF and MP2. The series of methods MP2, MP3, MP4, CCSD, and CCSD(T) shows an oscillatory behavior for the Au···Au interaction energy of (XAuPH₃)₂ (Ref. [7], Fig. 9) and for the Au···Au distance of the A-frame system S(AuPH₃)₂ (Ref. [3], Fig. 2).

Appropriate symmetry constraints were imposed during most of the calculations, and the rotation of the terminal –PH₃ ligands was inhibited. The latter approximation has been determined to have very little influence on the calculated structures [3].

Since analytical Hessians at the MP2 level are unavailable in the Turbomole [18, 19] program, the minima were verified by introducing small perturbations into the final geometries, and repeating completely unconstrained optimizations from these perturbed starting points at the RI-MP2 level. If the systems returned into the minima obtained with symmetry restrictions, this was taken as additional confirmation that true minima had been obtained.

The Turbomole [18, 19] program package was used for most of the calculations. Some of the smallest systems were calculated with Gaussian 94 [20].

Table 1. Basis sets and effective core potentials (ECP) used in this work

Element	Basis	ECP	Exponents of polarization functions	References
H	(4s 1p)/ [2s 1p]	–	$\alpha_p = 0.8$	31
B	(4s 4p 1d)/ [2s 2p 1d]	Bergner	$\alpha_d = 0.388$	11, 12
P	(4s 4p 1d)/ [2s 2p 1d]	Bergner	$\alpha_d = 0.34$	11, 12
Au	(8s 7p 6d 2f)/ [6s 5p 3d 2f]	Andrae	$\alpha_f = 1.19, 0.2$	10

Table 2. Exponents of the auxiliary basis sets used in this work. All auxiliary basis sets were even-tempered (ratio = 3.0) and fully uncontracted

Element	<i>l</i> value	No. of functions	Highest exponent	Lowest exponent
H	<i>s</i>	6	26.7230000	0.1099712
	<i>p</i>	6	14.1615000	0.0582778
	<i>d</i>	2	1.6000000	0.5333333
B	<i>s</i>	5	3.3811200	0.0417422
	<i>p</i>	5	7.0904730	0.0875367
	<i>d</i>	6	10.7998260	0.0444437
	<i>f</i>	5	5.7879130	0.0714557
P	<i>s</i>	6	13.4446160	0.0553276
	<i>p</i>	6	8.0055290	0.0329446
	<i>d</i>	6	7.0623080	0.0290630
	<i>f</i>	4	1.6232210	0.0601193
Au	<i>s</i>	9	40.2305980	0.0061318
	<i>p</i>	8	28.7249640	0.0131344
	<i>d</i>	8	24.2592480	0.0110925
	<i>f</i>	8	21.3052990	0.0097418
	<i>g</i>	8	21.1152990	0.0096549
	<i>h</i>	7	9.6096650	0.0131820

3 Systems studied

In the periodic table, boron is situated immediately to the left of carbon, and has three valence electrons. Thus the borohydride ion, BH₄[–], is isoelectronic with methane, CH₄. The phosphinegold ligand, –AuPH₃, is isolobal with hydrogen, and thus one could imagine the creation of a series of substituted borohydrides, BH₃AuPH₃[–], BH₂(AuPH₃)₂[–], BH(AuPH₃)₃[–], and B(AuPH₃)₄[–]. These would be isoelectronic with the experimentally known carbon-centered systems (the experimental systems have –PPh₃ ligands instead of –PH₃ and may have substituents other than hydrogen at the central atom, without breaking the overall analogy). Since an octet of electrons is present around the boron atom in these systems, we shall call them the “eight-electron, four-ligand” series in the following discussion.

The smallest electroneutral hydride of boron is BH₃. It has been seen in matrices [21], but normally dimerizes into the diborane, B₂H₆, molecule. Thus an alternative series of “gilded” boranes can be built from BH₃, in the hope that the bulkier phosphinegold ligands create a barrier to dimerization. This series would include BH₂AuPH₃, BH(AuPH₃)₂, and B(AuPH₃)₃, forming the uncharged, but electronically unsaturated “six-electron, three-ligand” series.

By protonating or aurating the latter, a “six-electron, four-ligand” series will be obtained, made up of BH₃AuPH₃⁺, BH₂(AuPH₃)₂⁺, BH(AuPH₃)₃⁺, and B(AuPH₃)₄⁺. Analogously, by removing a ligand from the eight-electron, four-ligand species, we will complete the scene with the “eight-electron, three-ligand” dianions BH₂AuPH₃^{2–}, BH(AuPH₃)₂^{2–}, and B(AuPH₃)₃^{2–}.

At a casual inspection, the four-ligand species B(AuPH₃)₄⁺ and B(AuPH₃)₄[–] might be assumed to have tetrahedral *T_d* symmetry. From the structure of the carbon analogs it is known, however, that the gold–gold attractions can cause it to distort either to a *C_{3v}* (three short and three long Au···Au distances) or even to a tetragonal pyramidal *C_{4v}* configuration. All these, as well as some other possibilities, were investigated here, in order to find out their relative stabilities.

Finally, the *C_{4v}* species can be protonated at the top [3], in analogy with the experimentally known C(AuPPh₃)₄, leading to the five-coordinated HB(AuPH₃)₄. Granted the stability of the known isoelectronic H[C(AuPPh₃)₄]⁺, this is an interesting candidate.

For gold-substituted diboranes, the two isomers of B₂H₄(AuPPh₃)₂ were studied, in which the gold atoms substitute the hydrogens either in the terminal or in the bridging positions, respectively. All the systems studied in this work are summarized in Table 3.

4 Structures

4.1 The unsubstituted borohydrides

These molecules and ions can be thought of as reference points for all the subsequent systems, and their properties are briefly reviewed here. Starting from the positively

Table 3. All systems studied in this work and their full symmetries

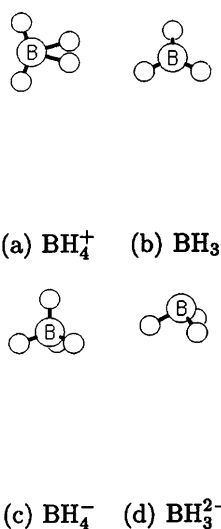
Au count	Charge: +1		0	-1	-2
	Six-electron		Eight-electron		
	Four-ligand	Three-ligand	Four-ligand	Three-ligand	
0	BH ₄ ⁺ (C _{2v})	BH ₃ (D _{3h})	BH ₄ ⁻ (T _d)	BH ₃ ²⁻ (C _{3v})	
1	BH ₃ AuPH ₃ ⁺ (C _s)	BH ₂ AuPH ₃ (C _s)	BH ₃ AuPH ₃ ⁻ (C ₃)	BH ₂ AuPH ₃ ²⁻ (C _s)	
2	BH ₂ (AuPH ₃) ₂ ⁺ (C _{2v})	BH(AuPH ₃) ₂ (C _{2v}) H ₂ B(AuPH ₃) ₂ BH ₂ (C _{2h}) H ₂ BH ₂ B(AuPH ₃) ₂ (C _{2v})	BH ₂ (AuPH ₃) ₂ ⁻ (C _{2v})	BH(AuPH ₃) ₂ ²⁻ (n/c)	
3	BH(AuPH ₃) ₃ ⁺ (C _s)	B(AuPH ₃) ₃ (C _{3v})	BH(AuPH ₃) ₃ ⁻ (C _{3v})	B(AuPH ₃) ₃ ²⁻ (C _{3v})	
4	B(AuPH ₃) ₄ ⁺ (C _{4v} , C _{3v} , C _{2v}) BH(AuPH ₃) ₄ ²⁺ (C ₁)		B(AuPH ₃) ₄ ⁻ (C _{3v} , C _{4v} , C _s) BH(AuPH ₃) ₄ (C _{4v}) PH ₃ -B(AuPH ₃) ₄ (C _s)		

charged end of the series, BH₄⁺ is known from mass spectroscopy as a reaction intermediate [22], but has not been structurally characterized experimentally. Calculations suggest a rather unusual planar structure (Fig. 1a) and it can be described as a complex between the BH₂⁺ ion and a dihydrogen molecule [23, 24].

The borane, BH₃, (Fig. 1b) is known only in the gas phase [25] and in matrices [21] and is flat (D_{3h}). The common borohydride species is the dimer B₂H₆ (diborane).

The “borohydride anion” BH₄⁻ (Fig. 1c) is commonplace. It is a tetrahedral, methane-like closed-shell ion without any surprising computational characteristics.

The BH₃²⁻ dianion (Fig. 1d) has an electron structure analogous to that of ammonia, and assumes a trigonal pyramidal geometry. Experimentally it has been observed as a reaction intermediate in solutions [26].

**Fig. 1a–d.** The four unsubstituted borohydrides

4.2 The six-electron, four-ligand series

The members of this cationic series “lack” two electrons relative to the octet rule for the central atom, and the six remaining ones cannot properly support four classical chemical bonds. This leads to distortions from the higher symmetries which would be otherwise obtained. Several of the systems would have degenerate highest occupied molecular orbitals (HOMOs) and would become triplets if the geometry were restricted to high symmetry.

All the structures (Fig. 2) are related to that of BH₄⁺, with the gold atoms initially entering the “H₂” part of the ion, and forming a rather short (253–255 pm) Au···Au distance, essentially a phosphinegold analog of the H₂ molecule. The structures are rather distorted, and, as discussed later, have high heats of formation. The B-H and B-Au bond lengths are fairly typical for this class of systems (see also Table 4), except for BH₃AuPH₃⁺, which is better characterized as a charge-dipole complex of BH₃ and AuPH₃⁺, with an Au-B bond length of 234 pm (200–210 pm is typical for these species).

A Mulliken population analysis of BH(AuPH₃)₃⁺ suggests that there is a significant overlap population

(0.81 electrons) between the two close-lying gold atoms. This fact will be evaluated further later, in the discussion of B(AuPH₃)₃. Similar nearly binding situations can be recognized in other species as well.

B(AuPH₃)₄⁺ has several local minima on its potential-energy surface (PES), with the one depicted on Fig. 2d having the lowest energy. The other two are 150 kJ/mol (Fig. 2e) and 110 kJ/mol (Fig. 2f) higher in energy.

The HB(AuPH₃)₄²⁺ protonated tetrapod would have to use its six valence electrons on boron to support five chemical bonds – apparently not an easy proposition. Geometry optimization of this species leads to several local minima, with the lowest one found illustrated in Fig. 2g.

4.3 The six-electron, three-ligand series

In this electroneutral series, all three species are closed-shell singlets at the highest symmetries; however, since it is well known that BH₃ dimerizes, one would not exclude chances of similar behavior in these systems as

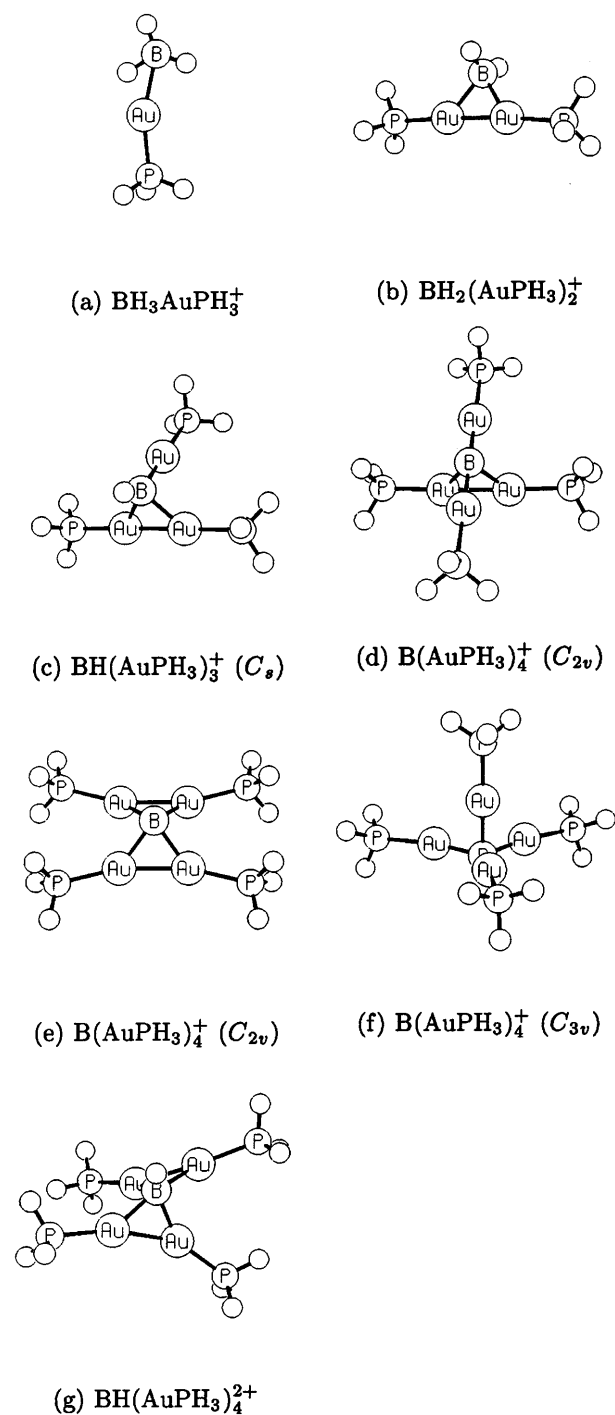


Fig. 2a–g. The six-electron, four-ligand cations

well. Possible dimerization is beyond the scope of this study, however.

BH_2AuPH_3 is a singlet with a trigonal planar arrangement of ligands around the boron (Fig. 3a). The triplet, at over 2.7 eV higher in energy, would be pyramidal at boron. Formally, the dimers of this species would be the diaurated diboranes, which are discussed in some detail later.

The digold $\text{BH}(\text{AuPH}_3)_2$ is a C_{2v} “A-frame” (Fig. 3b), so named because of its shape and it is re-

minescent of the analogous carbon-, nitrogen-, and sulfur-centered systems [3]. The MP2 gold–gold distance, 312.2 pm, is shortened from 371.7 pm in the HF geometry, suggesting the presence of aurophilic attraction also in this type of electron-deficient system. It is slightly longer than the typical distances (292–305 pm) in the A-frames studied earlier [3], however. Note that the MP2 Au–B–Au angle is 101.0° instead of 120° .

$\text{B}(\text{AuPH}_3)_3$ is again flat (nearly D_{3h} BAu_3 core, C_{3v} overall due to the phosphine groups, Fig. 3c), similar to BH_3 . Apparently the gold–gold attraction cannot overcome the overall repulsion determining the structure of this type of species, and the system will not assume a pyramidal structure. Even though there is no lone pair readily available on the boron for bonding to a fourth ligand, this species attracts a proton with an extraordinary proton affinity (PA) of 1137 kJ/mol. The resulting B–H distance is 120 pm, a value typical for these compounds, while the system itself distorts heavily, forming $\text{BH}(\text{AuPH}_3)_3^+$. The additional stabilization could be provided by the formation of a covalent Au–Au bond, as suggested by the significant Mulliken overlap population between the gold atoms in the protonated species.

The value of the PA, 1137 kJ/mol, is nearly as large as the value of 1213 kJ/mol calculated at the same level of approximation for $\text{C}(\text{AuPH}_3)_4$ [3]. Note that the PA of the “proton sponge” molecule 1,8-bis(dimethylamino)naphthalene is at most slightly above 1000 kJ/mol [27, 28].

4.4 The eight-electron, four-ligand series

This series of negatively charged ions contains the isoelectronic/isolobal analogs of methane and its gold-substituted derivatives. Since the octet rule around the central atom is now satisfied, all members of the series are singlet closed-shell anions without symmetry-breaking.

$\text{BH}_3\text{AuPH}_3^-$ (Fig. 4a) dissociates into PH_3 and BH_3Au^- at the HF level, but does not when the MP2 approach is employed. The Au–P bond is elongated and has a length of 257.4 pm (typical Au–P bond length is 230–235 pm). Apparently, electron correlation plays an important role in the stability of this anion. The local geometry is nearly tetrahedral at both the $-\text{BH}_3$ and $-\text{PH}_3$ ends.

The $\text{BH}_2(\text{AuPH}_3)_2^-$ A-frame (Fig. 4b) is very similar to its carbon-centered counterpart [3] with nearly-linear B–Au–P bond angles and a 282.9 pm Au \cdots Au distance. However, just as in $\text{BH}_3\text{AuPH}_3^-$, the PH_3 ligands separate themselves from the molecule if no electron correlation is accounted for.

The $\text{BH}(\text{AuPH}_3)_3^-$ capped tripod (Fig. 4c) has relatively small (85.7°) Au–B–Au angles, while the Au \cdots Au distances remain in the typical range for these systems (284.3 pm). The ligands remain bound at the HF level as well, with the Au–B–Au angles opening up to 99.5° . Thus aurophilic attraction is a major contributor to the geometry of this species.

The $\text{B}(\text{AuPH}_3)_4^-$ anion can, again, assume either T_d , C_{3v} , C_{4v} , or even lower symmetries. The C_{4v} and both of

Table 4. Main geometric parameters of the systems studied resolution of identity–second order Møller–Plesset (RI–MP2) level. For nonequivalent atoms, the parameters for axial (or otherwise unique) ones are listed first, followed by equatorial (or otherwise nonunique) ones

System	Symmetry	B-H (pm)	B-Au (pm)	Au···Au (pm)	Au-P (pm)	Au-B-Au (deg.)	B-Au-P (deg.)
BH ₄ ⁺	C _{2v}	118.3 ^a 145.1 ^b					
BH ₃ AuPH ₃ ⁺	C _s	118.8 119.4 129.7	234.0		230.5		162.6
BH ₂ (AuPH ₃) ₂ ⁺	C _{2v}	120.0	214.5	254.6	236.2	72.8	129.7
BH(AuPH ₃) ₃ ⁺	C _s	120.1	202.5 212.9	253.3 303.1	240.3 234.8	93.7 73.0	178.4 127.1
B(AuPH ₃) ₄ ⁺	C _{2v}		201.5 216.6	252.6 294.2	238.9 233.4	71.4 89.4	178.8 123.0
BH(AuPH ₃) ₄ ²⁺	C ₁	120.4	214–216	260–295	236	74–87	141–151
BH ₃	D _{3h}	120.2					
BH ₂ AuPH ₃	C _s	120.7	204.1		244.3		179.6
BH(AuPH ₃) ₂	C _{2v}	120.3	202.2	312.1	244.4	101.0	176.0
B(AuPH ₃) ₃	C _{3v}		200.2	346.8	243.9	120.0	179.3
BH ₄ ⁻	T _d	125.1					
BH ₃ AuPH ₃ ⁻	C ₃	123.4	213.9		257.4		180.0
BH ₂ (AuPH ₃) ₂ ⁻	C _{2v}		211.1	282.9	244.1	84.2	177.7
BH(AuPH ₃) ₃ ⁻	C _{3v}	121.1	209.1	284.3	238.0	85.7	176.8
B(AuPH ₃) ₄ ⁻	C _s		204.6 201.4 204.5	283.7 370.8 294.3	235.2 235.2 235.3	86.1 132.0 92.0	179.3 179.5 177.1
BH(AuPH ₃) ₄	C _{4v}	122.0	214.2	276.0	235.4	80.3	175.9
PH ₃ -B(AuPH ₃) ₄ ⁺ ^c	C _s	193.3 ^d	212.7	279.8	234.9	82.2	178.5
BH ₃ ²⁻	C _{3v}	134.3					
BH ₂ AuPH ₃ ²⁻	C _s	121.7	203.7		241.3		175.0
B(AuPH ₃) ₃ ²⁻	C _{3v}		209.6	279.5	234.7	83.6	171.0
H ₂ B(AuPH ₃) ₂ BH ₂	C _{2h}	120.8	217.3	255.1	232.2	71.9	125.9
H ₂ BH ₂ B(AuPH ₃) ₂	C _{2v}	131.9 ^e	204.3	315.2	241.0	100.9	174.3

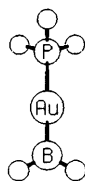
^a The hydrogens bound to B

^b The hydrogens in the “H₂” part

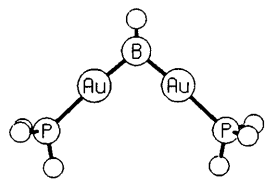
^c Average values for most geometric parameters

^d B–P distance

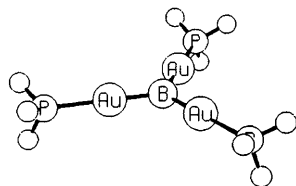
^e To a bridging hydrogen



(a) BH₂AuPH₃



(b) BH(AuPH₃)₂



(c) B(AuPH₃)₃

Fig. 3a–c. The six-electron, three-ligand molecules

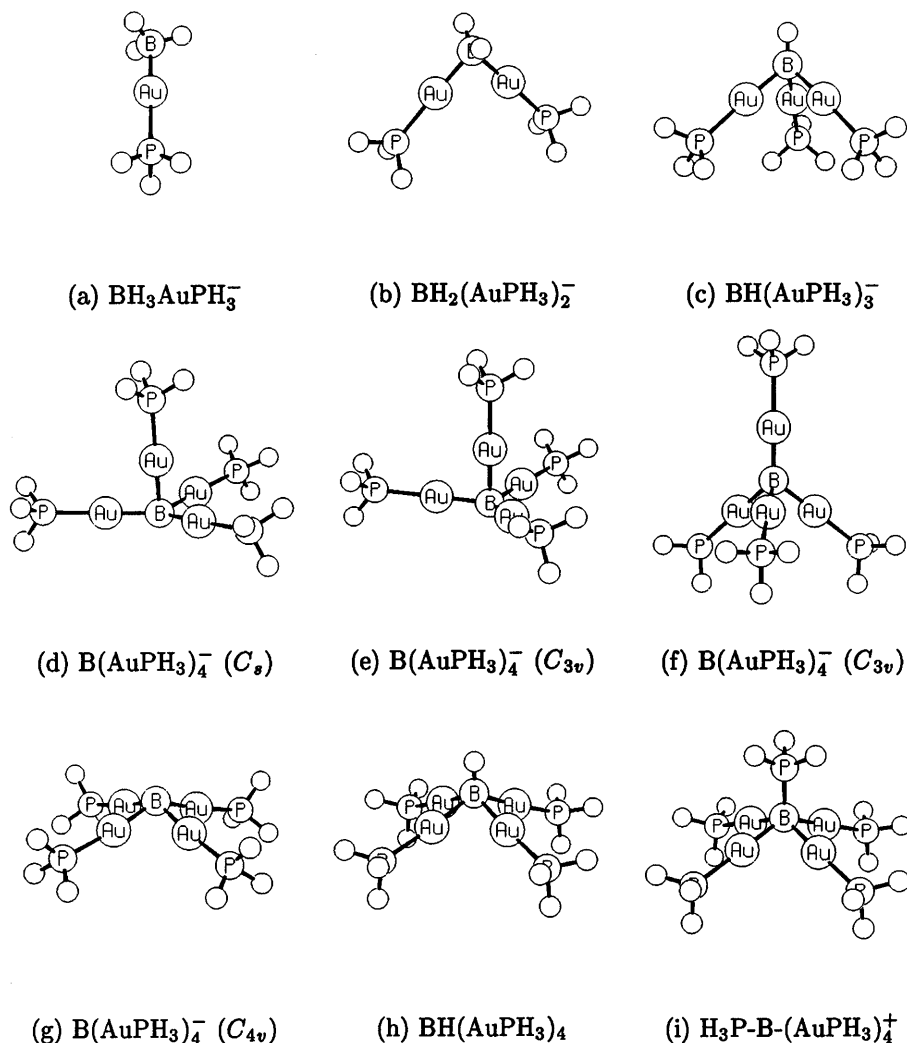
the C_{3v} species appear to be minima on the PES. The T_d structure is not a stationary point, and will distort into a

C_{3v} configuration, revealing the role of aurophilic attraction in the determination of the geometry of this species. The lowest-energy minimum appears to be a C_s structure which can be viewed as a slightly distorted C_{3v} case where the equatorial ligands are bent “up” (i.e. towards the axial one) and two of them have moved slightly closer to each other (Fig. 4d). The C_{3v} structure depicted in Fig. 4e is only 5 kJ/mol higher. The other C_{3v} structure (Fig. 4f) is 18 kJ/mol higher, and the C_{4v} structure (Fig. 4g) is 28 kJ/mol higher than the lowest-energy C_s configuration.

Protonation of B(AuPH₃)₄⁻ leads to the electroneutral HB(AuPH₃)₄ (Fig. 4h) with the release of 1553 kJ/mol. It should be noted that this is not a PA of a neutral species, and should thus not be compared with them. The Au–B–Au angle is 80.3°, slightly down from 83.1° in the C_{4v} B(AuPH₃)₄⁻. Even at the HF level, the Au–B–Au angle only straightens to 83.8°, indicating that in this case aurophilic attraction does not play a major role in determining the structure of this species.

PH₃-B(AuPH₃)₄⁺ (Fig. 4i) is analogous to the only experimentally known system [5] among the ones studied in this work, (C_y3P)B[Au(PPh₃)₄]⁺. The axial –PH₃ ligand donates an electron pair to the central atom, completing the eight-electron requirement for it, and thus placing it in the “eight-electron” series. Indeed, the system possesses a regular, nearly C_{4v} local symmetry at the boron center, broken into C_s because of the threefold

Fig. 4a-i. The eight-electron, four-ligand anions



symmetry at the axial ligand. The main geometric parameters, the average $\text{Au}\cdots\text{Au}$ distance (280 pm) and Au-B-Au angle (82°), compare very well with the experimental values [5] (282 pm and 81° , respectively).

The structure at the five-coordinated boron atom is not affected too much by the van der Waals interactions between the gold atoms. At the HF level, where these interactions are essentially missing, the Au-B-Au angle is only minimally straightened, from 82° to 84.5° . One could thus conclude that the structure at the central atom is primarily determined by the repulsion of electron pairs, and not just by the aurophilic attraction forces.

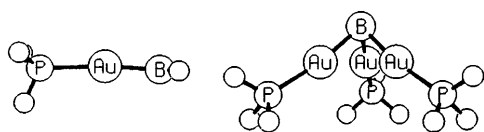
4.5 The eight-electron, three-ligand series

This series consists of doubly charged anions, which are unlikely to exist in free form and cause problems when treated quantum-chemically. In all cases, the allowable number of self-consistent field (SCF) iterations had to be increased in order to achieve convergence of the calculation. For the $\text{BH}(\text{AuPH}_3)_2^{2-}$ system, we were unable to achieve convergence of the SCF.

The $\text{BH}_2\text{AuPH}_3^{2-}$ and $\text{B}(\text{AuPH}_3)_3^{2-}$ dianions (Fig. 5) have the expected geometric forms. For the latter, at the HF level the geometry of the BAu_3 core is essentially flat; thus, the pyramidity is primarily driven by the gold-gold attractions.

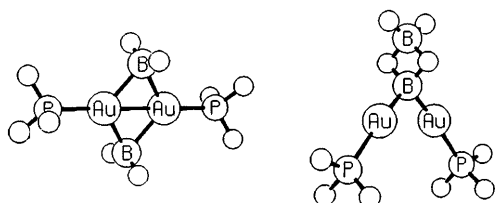
Of the diaurated diboranes, $\text{H}_4\text{B}_2(\text{AuPH}_3)_2$, those with two phosphinegold groups in the bridging position, $\text{H}_2\text{B}(\text{AuPH}_3)_2\text{BH}_2$ (Fig. 6a) or both in a terminal position, $\text{H}_2\text{BH}_2\text{B}(\text{AuPH}_3)_2$ (Fig. 6b) were investigated. The latter turned out to be 141 kJ/mol lower in energy. Concomitantly, the $\text{Au}\cdots\text{Au}$ distance in the bridged system is only 255 pm, and is considerably lower than the 315 pm in the terminal case. The short Au-Au distance is comparable to that in an Au_2 molecule (249 pm), within the approximations used in this study. The experimental value for Au_2 is 247.2 pm [29].

Typically, we would have expected a big Au-Au -induced stabilization of the bridged system, given the short Au-Au distance. Apparently, however, the electron-deficient nature of the chemical bonds in a diborane environment does not allow enough flexibility for the attraction to have its full force. The Au-Au distance is shortened from 264 pm in a HF calculation to 255 pm at



(a) $\text{BH}_2\text{AuPH}_3^{2-}$ (b) $\text{B}(\text{AuPH}_3)_3^{2-}$

Fig. 5a, b. The eight-electron, three-ligand dianions



(a) $\text{H}_2\text{B}(\text{AuPH}_3)_2\text{BH}_2$ (b) $\text{H}_2\text{BH}_2\text{B}(\text{AuPH}_3)_2$

Fig. 6a, b. The aurated diboranes

the MP2 level. Note that the HF distance is very short, indicating a covalent bond. One could consider the system as consisting of an Au_2 molecule (ignoring the phosphine ligands for a moment) and two BH_2 fragments. The former would contribute one in-phase orbital and two electrons to form the bonds, and the latter would contribute one orbital and one electron each. By symmetry, we obtain one bonding MO and one which is nonbonding between the Au_2 and BH_2 fragments, and is antibonding relative to the two BH_2 fragments, resulting in a relatively weak bond overall. The third MO, which is antibonding relative to the Au_2 and BH_2 fragments, is not filled.

In the terminally substituted case, on the other hand, the diborane system appears to be too rigid to allow bending of the “A-frame” part of the molecule for a typical aurophilically shortened $\text{Au} \cdots \text{Au}$ distance. Even as it stands, the distance is significantly decreased by the electron correlation: from 372 pm at the HF level to 315 pm in MP2.

With Mulliken population analysis it was found that the interatomic overlap populations in the bridge-substituted case suggest a partially covalent character of the interaction. There are 0.3825 electrons in the overlap orbitals, to be compared with an overlap of 0.4165 between Au and each of the borons. In the terminally substituted case the corresponding Au-Au overlap population is only 0.0982.

Such a transition from the correlation-induced aurophilic attraction at $R(\text{Au}-\text{Au}) \simeq 270\text{--}320$ pm to an essentially covalent bond at $R(\text{Au}-\text{Au}) \simeq 247\text{--}260$ pm would be fairly natural. For a phenomenological theory of this transition, see Eq. (24) and Fig. 36 of Ref. [4] or

Fig. 5 of Ref. [3]. Such primarily covalent bonds are shown in Figs. 2b–e, g and 6a.

Of all the systems studied here, these may be of most interest to synthetic chemists. Granted the paucity of experimentally known Au-B bonds, the synthesis of substituted diboranes might be an interesting possibility.

5 Energetics

5.1 Heats of formation

In Table 5 we have collected the calculated values for the heats of formation of the compounds studied. In the first column these are given as gas-phase ΔH_f at 0 K, out of constituent elements in their standard states, without vibrational corrections. For the ions, they implicitly include the ionization energies of hypothetical electro-neutral reaction intermediates. Experimental atomization energies were included in the calculations.

In the second column, we give the calculated enthalpies of the formation reactions, ΔH_{rxn} , relative to gas-phase boron atoms, gold atoms, H_2 molecules, and PH_3 molecules. For cations, the corresponding number of protons (H^+ ions) is included instead of H_2 molecules. For anions, H^- ions are included in the same way.

In the third column, the heat of formation given in the first column is divided by the number of gold atoms, which is taken as an estimate of the size (and thus the number of chemical bonds) in the molecule or ion. This

Table 5. Heats of formation (kJ/mol) of the systems studied

System	ΔH_f (gas phase)	ΔH_{rxn}^a	$\Delta H_f/N_{\text{Au}}$
BH_4^+	992.4	-1102.6	–
$\text{BH}_3\text{AuPH}_3^+$	834.7	-1631.8	834.7
$\text{BH}_2(\text{AuPH}_3)_2^+$	742.2	-2095.8	371.1
$\text{BH}(\text{AuPH}_3)_3^+$	737.3	-2472.2	245.8
$\text{B}(\text{AuPH}_3)_4^+$	693.3	-2887.7	173.3
$\text{BH}(\text{AuPH}_3)_4^{2+}$	1494.7	-3616.3	373.7
BH_3	77.8	-487.2	–
BH_2AuPH_3	208.3	-728.2	208.3
$\text{BH}(\text{AuPH}_3)_2$	299.0	-1009.0	149.5
$\text{B}(\text{AuPH}_3)_3$	357.8	-1321.7	119.3
BH_4^-	-37.5	-2046.5	–
$\text{BH}_3\text{AuPH}_3^-$	70.9	-2309.6	70.9
$\text{BH}_2(\text{AuPH}_3)_2^-$	121.1	-2631.0	60.5
$\text{BH}(\text{AuPH}_3)_3^-$	109.8	-3013.7	36.6
$\text{B}(\text{AuPH}_3)_4^-$	106.7	-3388.4	26.7
$\text{BH}(\text{AuPH}_3)_4$	93.8	-1957.2	23.4
$\text{PH}_3\text{-B}(\text{AuPH}_3)_4^{+b}$	480.2	-3106.2	120.0
BH_3^{2-}	1021.6	-2431.4	–
$\text{BH}_2\text{AuPH}_3^{2-}$	594.2	-3230.4	594.2
$\text{B}(\text{AuPH}_3)_3^{2-}$	480.0	-4087.6	160.0
$\text{H}_2\text{B}(\text{AuPH}_3)_2\text{BH}_2$	324.0	-1549.0	162.0
$\text{H}_2\text{BH}_2\text{B}(\text{AuPH}_3)_2$	183.3	-1689.7	91.7

^a For the reaction from $\text{B}(\text{g})$, $\text{Au}(\text{g})$, H_2 , H^+ , H^- , PH_3

^b RI-MP2 energy was used for the calculation

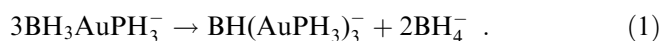
gives a rough idea of the energy content of the system irrespective of its size.

The heats of formation are all positive, with the exception of BH_4^- . From this point of view, we support the experimental findings that, in general, systems of this type are uncommon and most attempts to synthesize them have been unsuccessful. Besides these two systems, the only species with a relatively low heat of formation per gold atom, and thus potentially accessible synthetically, are the anions belonging to the eight-electron, four-ligand series, as well as the electroneutral $\text{HB}(\text{AuPH}_4)_4$. The terminally “gilded” diborane is also not too far removed from these systems, followed by some members of the six-electron, three-ligand series. $\text{PH}_3\text{BAu}(\text{PH}_3)_4^+$, which is also known experimentally, has an even higher heat of formation. This adds hope that the other systems could be experimentally accessible as well.

5.2 Auophilic contributions to stability

The auophilic energy contributions for systems containing two or more gold atoms were estimated on the basis of isodesmic reactions, which preserve the charge of individual species, as well as the number and character of the chemical bonds. As studied earlier [3], the change in correlation energy in such reactions correlates best with gold–gold distances, and is therefore used here as an estimate of the auophilic contribution to the stability of these species.

A typical isodesmic reaction on which these estimates are based would be, for the case of $\text{BH}(\text{AuPH}_3)_3^-$



Wherever possible, the number of ligands and the total charge were kept the same in all species involved in such equations.

The auophilic contribution to the stability of the system, E_{aur} , was computed as follows:

$$E_{\text{aur}} = \Delta E_{\text{corr}}^{\text{MP2}} / N_{\text{Au}\cdots\text{Au}} \quad (2)$$

where $\Delta E_{\text{corr}}^{\text{MP2}}$ is the change in MP2 correlation energy in the isodesmic reaction, and $N_{\text{Au}\cdots\text{Au}}$ is the number of $\text{Au}\cdots\text{Au}$ contacts in the system. The values thus obtained include correlation differential effects due to, for instance, changes in bond lengths and bond energies between the species participating in the isodesmic reactions of the type of described by Eq. (1). While this introduces some uncertainty into the results, our comparisons with alternative formulations, including some which did not allow for geometry relaxation, gave preference to the definition of Eq. (2) for E_{aur} over the other options. The numerical values are presented in Table 6.

From our earlier studies [3], the typical range for this type of auophilic interaction energy is in the range of 30–100 kJ/mol per Au–Au pair. As can be seen from the data, in these systems the auophilic contributions to the stability are much larger, reaching over 150 kJ/mol for some of the systems. The experimentally known $\text{PH}_3\text{B}(\text{AuPH}_3)_4^+$ also has a quite low calculated au-

Table 6. Estimates of auophilic contributions to the stability of the systems studied (kJ/mol)

System	E_{aur}	$N_{\text{Au}\cdots\text{Au}}$	$E_{\text{aur}}/N_{\text{Au}\cdots\text{Au}}$
$\text{BH}_2(\text{AuPH}_3)_2^+$	−179.2	1	−179.2
$\text{BH}(\text{AuPH}_3)_3^+$	−382.9	3	−127.6
$\text{B}(\text{AuPH}_3)_4^+$	−627.8	6	−104.6
$\text{BH}(\text{AuPH}_3)_4^{2+}$	−362.6	6	−60.4
$\text{BH}(\text{AuPH}_3)_2$	−70.1	1	−70.1
$\text{B}(\text{AuPH}_3)_3$	−138.5	3	−46.2
$\text{BH}_2(\text{AuPH}_3)_2^-$	−67.6	1	−67.6
$\text{BH}(\text{AuPH}_3)_3^-$	−189.0	3	−63.0
$\text{B}(\text{AuPH}_3)_4^-$	−294.7	6	−49.1
$\text{BH}(\text{AuPH}_3)_4$	−145.7	6	−24.3
$\text{PH}_3\text{-B}(\text{AuPH}_3)_4^{\text{a}}$	−118.5	6	−19.7
$\text{B}(\text{AuPH}_3)_3^{2-}$	−621.7	3	−207.2
$\text{H}_2\text{B}(\text{AuPH}_3)_2\text{BH}_2$	201.5	1	201.5
$\text{H}_2\text{BH}_2\text{B}(\text{AuPH}_3)_2$	426.1	1	426.1

^a RI-MP2 energy was used for the calculation

ophilic stabilization. This may bear relation to its geometry being quite insensitive to the inclusion of correlation effects, as noted earlier. The apparent lack of auophilic influence on the structure and stability of $\text{PH}_3\text{B}(\text{AuPH}_3)_4^+$ may be explained by the capacity of boron to participate in widely varying covalent bonding situations [30].

The extreme values for the auophilic contributions occur at the ends of the range of the systems studied: the cations and the dianions. This shows, on one hand, that if these systems were ever synthesized, their stability would be primarily due to auophilic effects. On the other hand, this points to the deficiency of the method used here for calculating the auophilic contributions: the monoaurated systems are relatively unstable, as pointed out in Sect. 4, and therefore may indicate artificially large auophilic contributions.

The disubstituted diboranes do not exhibit an auophilic stabilization when calculated by this method: a destabilizing effect is found instead. This may be related to the unusual $\text{Au}\cdots\text{Au}$ distances present in these compounds, as well as possible compensation for the gain from auophilic interactions by the strain in the electron-deficient three-centered bonds in these molecules.

6 Conclusions

The quantum-chemical methods used for the work reproduces the structural parameters of the few experimentally known systems fairly well, and thus remains the recommended relatively inexpensive way to approach the auophilic systems. New and improved ways of estimating the auophilic contributions to the stability may, however, be required.

Boron-centered aurated molecules and ions still represent a challenge to the synthetic inorganic chemists. The current work helps to shed some light on the reasons for that. The gas-phase heats of formation of these

systems from the elements are positive, the only exceptions being the systems which are already known experimentally. On the other hand, aurophilic (or possibly covalent, as discussed previously) contributions to the stability of these molecules and ions are unusually large, increasing the chances of experimental accessibility to them.

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Appendix

In order to estimate the trustworthiness of the results, structural and energetic data of several small molecules were calculated at the level of theory used in this work, and compared against the available experimental data. The numerical results can be found in Tables A1 and A2.

As one can see, the structural data are reproduced fairly well, and we should be able to trust the geometries obtained at this level up to 2–4 pm accuracy for covalent bonds and 2–3° for bond angles. The secondary Au···Au distances, as studied in Ref. [3], could be

Table A1. Comparison of structural data with experiment, in picometers and degrees

System	Datum	Calculation	Experiment	Error	Ref.
BH	R(B-H)	124	123	+1	29
B ₂	R(B-B)	162	159	+3	29
B ₂ H ₆	R(B-H _{bridge})	132	132	0	32
	R(B-H _{terminal})	120	119	+1	32
	∠(H-B-H _{bridge})	95.6	96.5	-0.9	32
	∠(H-B-H _{terminal})	122.8	121.8	+1.0	32
AuH	R(Au-B)	150	152	-2	29
AuB	R(Au-B)	189	193 ^a	-4	33
Au ₂	R(Au-B)	249	247	+2	29

^aAccurate calculation at DK (Douglas-Kroll)-CASPT2 level

Table A2. Comparison of energetic data with experiment (kJ/mol)

System	Datum ^a	Calculation	Experiment	Error	Error per bond	Ref.
B ₂	ΔH _f	882.4	830.5	+51.9	+51.9	34
	-D ₀	-248	-290	+42	+42	29
BH	ΔH _f	452.4	449.6	+2.8	+2.8	34
	-D ₀	-319	-330	+11	+11	29
BH ₃	ΔH _f	77.8	100.0	-22.2	-7.4	34
B ₂ H ₆	ΔH _f	-27.5	35.6	-63.1	-7.9	34
Au ₂	ΔH _f	484	515	-31	-31	34
AuH	ΔH _f	289	295	-6	-6	34
	-D ₀	-283	-311	+28	+28	29
AuB	-D ₀	-367	-347	-20	-20	29

^aDissociation energies, D₀, are listed with opposite sign in order to keep the signs of any systematic errors uniform

trusted to 10–15 pm accuracy, being perhaps too short rather than too long.

The energetic estimates for B-H bonds show deviations of up to 11 kJ/mol per bond, while the bonds containing gold are accurate up to about 30 kJ/mol. The B-B bond energies show larger deviations, but there are no such bonds in the molecules studied here. No experimental energetic data for Au-P bonds was readily available for checking the accuracy of these estimates. One should also keep in mind that no vibrational corrections have been applied to any of these values. Thus one could expect the heats of formation calculated in this work to be accurate to within 50–100 kJ/mol, with the accuracy decreasing as the number of gold atoms in the system increases.

Any errors made in estimating the energy of P-H bonds should not influence the accuracy, since the experimental heat of formation of PH₃ is included in all the calculated values for species containing the PH₃ ligand.

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