

Structure of  $E(\text{AuPH}_3)_4^+$ ,  $E = \text{N, P, As}$ :  $T_d$  or  $C_{4v}$ ?Jian Li<sup>†</sup> and Pekka Pyykkö<sup>\*</sup>

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Quasirelativistic pseudopotential methods at HF and MP2 levels are used for optimizing the geometry of the title compounds. The naked clusters  $\text{EM}_4^+$  ( $M = \text{H, Ag, Au}$ ) are also considered. In agreement with experiment,  $\text{N}(\text{AuPH}_3)_4^+$  is  $T_d$  and the  $\text{As}(\text{AuPH}_3)_4^+$  ion is a  $C_{4v}$  square pyramid with an apical As atom.  $\text{P}(\text{AuPH}_3)_4^+$  is predicted to favor  $C_{4v}$ . The calculated MP2  $\text{Au}\cdots\text{Au}$  distance for  $E = \text{As}$  is 296 (experimental 290) pm, and the  $\text{Au}-\text{As}-\text{Au}$  is angle  $69.1$  ( $70.7$ )°. The bonding is analyzed. The secondary  $\text{Au}\cdots\text{Au}$  bond is attributed to correlation, not  $5d6s6p$  hybridization.

## Introduction

Tetrahedral,  $sp^3$  hybridization is one of the basic tenets of tetravalent main group chemistry. While the quaternary arsonium cations,  $\text{AsR}_4^+$ , fulfil this expectation, Schmidbaur *et al.*<sup>1</sup> found, despite the chemical similarity of  $-\text{H}$ ,  $-\text{R}$ , and  $-\text{AuPR}_3$ , that the  $\text{As}(\text{AuPPh}_3)_4^+$  in tetrafluoroborates crystallize in a square-pyramidal,  $C_{4v}$  structure. The short, 290 pm intramolecular  $\text{Au}-\text{Au}$  distances suggest that the "aurophilic"  $\text{Au}\cdots\text{Au}$  attraction<sup>2</sup> plays a role in stabilizing the  $C_{4v}$  structure. We now carry out an ab initio analysis of the bonding in this series,  $E(\text{AuPH}_3)_4^+$ ,  $E = \text{N, P, As}$  (**1a-c**), respectively. The  $T_d$  and  $C_{4v}$  geometries are shown in Figure 1. The "naked" clusters  $\text{EAu}_4^+$ ,  $E = \text{N, P, As}$  (**2a-c**), are also considered.

The **1a**, first reported in ref 3, is approximately tetrahedral<sup>1,4</sup> while **1b** is so far unknown. All these compounds are particular cases of the centered clusters  $E(\text{AuL})_n^{m+}$ , first predicted for  $n = 6$  by Mingos.<sup>5</sup> The cations  $\text{C}(\text{AuPPh}_3)_5^+$ ,  $\text{C}(\text{AuPPh}_3)_6^{2+}$ ,  $\text{N}(\text{AuPPh}_3)_3^{2+}$ , and  $\text{P}(\text{AuPPh}_3)_5^{2+}$  have been made; see ref 6. The bonding in these centered clusters has been studied by relativistic discrete variational  $X\alpha^{6,7}$  and pseudopotential<sup>8</sup> methods. Pyykkö and Zhao<sup>8</sup> found the radial,  $X-\text{Au}$ , bonding to be predominant, for ligand-free  $\text{XAu}_n^{m+}$  clusters at HF level. Rösch *et al.*<sup>6,7</sup> found that the phosphines open the 5d shell and lead to tangential,  $\text{Au}-\text{Au}$ , bonding, as well, at the experimental  $\text{Au}-\text{Au}$  distance of 300.5 pm of  $\text{C}(\text{AuL})_6^{2+}$ .

At this, and larger distances (about 300–340 pm), even between closed-shell Au(I) systems, an "aurophilic attraction" of some 6–8 kcal/mol or 30 kJ/mol is empirically found.<sup>2</sup> While Hoffmann *et al.*<sup>9</sup> have attributed this attraction between  $d^{10}$  systems to  $spd$  hybridization, we<sup>10,11</sup> found no attraction at HF level and the correct attraction at MP2 and MP3 levels and

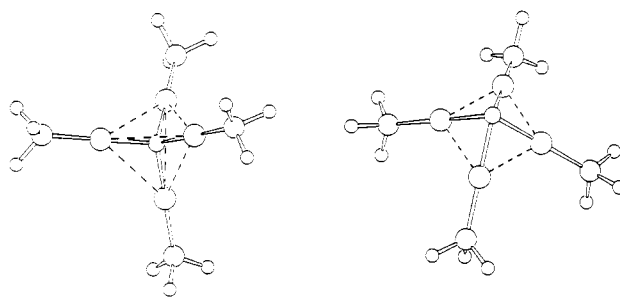


Figure 1. (a) The  $T_d$  and (b) the  $C_{4v}$  structures of  $E(\text{AuPH}_3)_4^+$ .

attributed it to correlation, enhanced by relativistic effects. In addition to the dimers  $(\text{ClAuPH}_3)_2$ , this attraction was needed to reproduce the  $\text{Au}\cdots\text{Au}$  distance in the new A-frame molecule  $\text{Se}(\text{AuPR}_3)_2$ .<sup>12</sup> The present  $\text{As}(\text{AuPR}_3)_4^+$  system could be seen as a pyramid, built of four such A-frames.

## Computational Details

The calculations were performed using Gaussian 90 and Gaussian 92 packages.<sup>13</sup> The 11 valence-electron (VE) quasirelativistic (QR) pseudopotential (PP) of Hay and Wadt<sup>14</sup> for Au, available under the "LANL1DZ" option, was employed. As and P were treated by the same set of pseudopotential. Two basis sets, "basis 1" and "basis 2", were adopted for geometry optimization and relative energy calculation, respectively. "Basis 1" corresponds to the minimal and double- $\zeta$  basis set associated with the pseudopotential,<sup>14</sup> that is,  $(3s3p3d)/[2s2p2d]$  for Au,  $(3s3p)/[2s2p]$  for As and P,  $(10s5p)/[3s2p]$  for N, and  $(4s)/[2s]$  for H. In "basis 2", the basis set of Au was augmented by a single  $f$ -type polarization function ( $\alpha = 0.20$ ), and  $d$ -type polarization functions ( $\alpha = 0.864, 0.340$  and  $0.293$ ) were added to N, P, and As, respectively.

For naked clusters  $\text{EAu}_4^+$  (**2**) geometries were fully optimized at HF and MP2 levels within the constraint of specified symmetries. Vibrational frequencies were calculated at the optimized stationary points by numerical evaluation of second derivatives of energy.

For  $E(\text{AuPH}_3)_4^+$  (**1**) two optimizations were carried out. In the first one only the  $E-\text{Au}$  distance and the  $\text{Au}-E-\text{Au}$  angle of the  $C_{4v}$  case were optimized. For  $\text{Au}-\text{P}$ ,  $\text{P}-\text{H}$ , and  $\text{Au}-\text{P}-\text{H}$ , the typical experiment values of 227.2 pm, 141.2 pm, and  $122.7^\circ$  were used, respectively. In the second, the latter three variables were optimized as well, within  $T_d$  or  $C_{4v}$ . The changes were minimal, except for  $\text{Au}-\text{P}$ , which grew from 227.2 to 253.7 pm for **1c** ( $C_{4v}$ ) at the MP2 level. The increase is attributed to the relatively small P basis in the optimization. This point is verified in Table I for  $\text{ClAuPH}_3$ . The "basis 1" gives too long  $\text{Au}-\text{P}$  and  $\text{Au}-\text{Cl}$ ,

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**Table I.** Effect of Basis on Calculated ClAuPH<sub>3</sub> Geometry with Distances in pm and Angles in deg

method	Au-P	Au-Cl	P-H	Au-P-H
basis 1 MP2	244.3	244.3	141.9	116.4
basis 2 HF	240.6	240.1	140.4	117.4
basis 2 MP2	235.6	238.7	141.7	118.5
basis 3 MP2 <sup>a</sup>	227.8	229.3	141.6	118.3
expt <sup>b</sup>	225	229		
expt <sup>c</sup>	224	229		

<sup>a</sup> 19-VE-PP and (8s6p5d1f)/[7s3p4d1f] basis for Au, (5s5p1d)/[3s3p1d] basis for P and Cl. See ref 11. <sup>b</sup> Reference 17. <sup>c</sup> Reference 18.

**Table II.** Optimized Bond Lengths (pm) and Angles (degrees) with Experimental Values in Parentheses

system	sym	E-M		∠M-E-M		M...M	
		HF	MP2	HF	MP2	HF	MP2
NAg <sub>4</sub> <sup>+</sup> (3a)	T <sub>d</sub>	214.9	214.9	a	a	350.9	350.9
	C <sub>4v</sub>	217.0	227.1	90.0	82.9	306.9	300.7
PAg <sub>4</sub> <sup>+</sup> (3b)	T <sub>d</sub>	251.5	248.0	a	a	410.8	405.0
	C <sub>4v</sub>	257.7	258.9	78.3	72.2	325.3	305.1
AsAg <sub>4</sub> <sup>+</sup> (3c)	T <sub>d</sub>	259.1	255.5	a	a	423.1	417.2
	C <sub>4v</sub>	265.7	265.5	75.7	69.9	326.2	304.3
NAu <sub>4</sub> <sup>+</sup> (2a)	T <sub>d</sub>	216.2	216.0	a	a	353.0	352.7
	C <sub>4v</sub>	225.4	228.2	81.4	79.1	293.9	290.6
PAu <sub>4</sub> <sup>+</sup> (2b)	T <sub>d</sub>	244.3	240.8	a	a	398.6	393.3
	C <sub>4v</sub>	253.5	255.5	72.5	69.1	299.9	289.7
AsAu <sub>4</sub> <sup>+</sup> (2c)	T <sub>d</sub>	251.1	247.6	a	a	410.0	404.3
	C <sub>4v</sub>	260.1	261.1	70.5	67.4	300.1	289.9
N(AuPH <sub>3</sub> ) <sub>4</sub> <sup>+</sup> (1a)	T <sub>d</sub>	214.7	213.2	a	a	350.5	348.1
	C <sub>4v</sub>	217.1	221.0	89.8	86.0	306.5	301.5
P(AuPH <sub>3</sub> ) <sub>4</sub> <sup>+</sup> (1b)	T <sub>d</sub>	245.9	242.7	a	a	401.5	396.3
	C <sub>4v</sub>	251.4	246.4	76.1	72.5	309.9	287.0
As(AuPH <sub>3</sub> ) <sub>4</sub> <sup>+</sup> (1c)	T <sub>d</sub>	253.2	250.0	a	a	413.5	408.3
	C <sub>4v</sub>	259.1	257.3	73.6	69.2	310.5	292.0
		258.6	260.9	72.6	69.1	306.1	296.1
		(250) <sup>e</sup>		(70.7) <sup>e</sup>		(290) <sup>e</sup>	

<sup>a</sup> The tetrahedral angle, 109.5°. <sup>b</sup> Average in N(AuPPh<sub>3</sub>)<sub>4</sub><sup>+</sup>F<sup>-</sup>. <sup>c</sup> Partial geometry optimization. <sup>d</sup> Full geometry optimization. <sup>e</sup> In As(AuPPh<sub>3</sub>)<sub>4</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup>.

a problem encountered by Schwerdtfeger *et al.*<sup>15</sup> "Basis 3" gives results close to experiment. Unfortunately, "basis 3" was too expensive for the present Au<sub>4</sub> systems. Pacchioni and Bagus<sup>16</sup> point out the importance of d-type polarization functions at P on the Pd-PH<sub>3</sub> bonding.

### Naked Clusters, EM<sub>4</sub><sup>+</sup>

**Symmetrical Structures.** The optimized geometries of 2a-c and the corresponding Ag clusters, 3a-c, are given in Table II.

The difference between the HF and MP2 E-M bond lengths for M = Ag and Au is a few picometers only, except for NAg<sub>4</sub><sup>+</sup> which is D<sub>4h</sub> in HF. Therefore the HF-level naked EAu<sub>4</sub><sup>+</sup> bond lengths in ref 8 are still credible. We note that N-Au > N-Ag but P-Au < P-Ag and As-Au < As-Ag, for the softer P and As. The Au...Au distances for 2 (C<sub>4v</sub>) are all about 290 pm while the Au-E-Au angles vary, suggesting aurophilic attraction already for 2.

The relative energies of the two symmetries are given in Table III. Data for EH<sub>4</sub><sup>+</sup> are included; for them the optimized C<sub>4v</sub> geometry is a saddle point. These hydrides strongly favor T<sub>d</sub>.

The correlation effects in MP2 level lower the C<sub>4v</sub> relative energy, and more so for Au than Ag, suggesting the importance of relativity. The difference between silver and gold is mainly a relativistic effect.<sup>19</sup> Only 3a prefers T<sub>d</sub> at MP2 level. Only 2c prefers C<sub>4v</sub> at HF level.

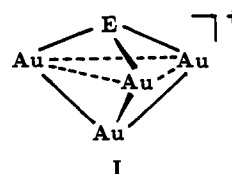
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**Table III.** Relative Energies, E(C<sub>4v</sub>) - E(T<sub>d</sub>), (kJ/mol) of EH<sub>4</sub><sup>+</sup>, EAu<sub>4</sub><sup>+</sup>, EAu<sub>4</sub><sup>+</sup>, and E(AuPH<sub>3</sub>)<sub>4</sub><sup>+</sup> (E = N, P, As)

system	HF			MP2	
	basis 1 <sup>a</sup>	basis 1 <sup>b</sup>	basis 2 <sup>b</sup>	basis 1 <sup>c</sup>	basis 2
NH <sub>4</sub> <sup>+</sup>	534.9	555.3		536.2 <sup>d</sup>	529.1 <sup>d</sup>
PH <sub>4</sub> <sup>+</sup>	508.7	443.0		453.6 <sup>d</sup>	352.7 <sup>d</sup>
AsH <sub>4</sub> <sup>+</sup>	459.7	409.1		401.2 <sup>d</sup>	333.3 <sup>d</sup>
NAg <sub>4</sub> <sup>+</sup> (3a)	81.3	75.7		40.1 <sup>d</sup>	38.3 <sup>d</sup>
PAg <sub>4</sub> <sup>+</sup> (3b)	54.0	44.0		-29.7 <sup>d</sup>	-39.8 <sup>d</sup>
AsAg <sub>4</sub> <sup>+</sup> (3c)	38.1	31.4		-55.2 <sup>d</sup>	-66.0 <sup>d</sup>
NAu <sub>4</sub> <sup>+</sup> (2a)	51.7	39.0		-34.9 <sup>d</sup>	-49.8 <sup>d</sup>
PAu <sub>4</sub> <sup>+</sup> (2b)	13.0	6.4		-113.9 <sup>d</sup>	-151.6 <sup>d</sup>
AsAu <sub>4</sub> <sup>+</sup> (2c)	-8.0	-12.6		-143.5 <sup>d</sup>	-192.5 <sup>d</sup>
N(AuPH <sub>3</sub> ) <sub>4</sub> <sup>+</sup> (1a)	82.8	80.7	85.0	50.7	53.4 <sup>b</sup>
P(AuPH <sub>3</sub> ) <sub>4</sub> <sup>+</sup> (1b)	53.6	48.2	51.6	-38.7	-49.3 <sup>b</sup>
As(AuPH <sub>3</sub> ) <sub>4</sub> <sup>+</sup> (1c)	40.2	30.8	38.9	-71.8	-76.0 <sup>b</sup>

<sup>a</sup> Energies are calculated at partially optimized HF level geometries. <sup>b</sup> Energies are calculated at fully optimized HF level geometries. <sup>c</sup> Energies are calculated at partially optimized MP2 level geometries. <sup>d</sup> Energies are calculated at fully optimized MP2 level geometries.

The possibility of a C<sub>3v</sub> geometry (structure I) was checked



and found to lie 9.9, 24.2 and 29.4 kJ/mol (at MP2 level) above the lowest-energy geometry for 2a-c, respectively.

**Distortions.** The C<sub>4v</sub> MP2 minimum of 2c is very shallow while 2a and 2b distort along one negative-frequency mode into C<sub>2v</sub> geometry. This negative-frequency mode corresponds to the pseudorotation from C<sub>4v</sub> to T<sub>d</sub>, as shown in Scheme I. The frequencies are given in Table IV. Departing from C<sub>4v</sub>, Scheme Ia, the bonds to gold atoms 2 and 4 go in and down, while the ones to atoms 1 and 3 go out and up. The diagonal Au...Au<sub>4</sub> distance decreases while the peripheral Au<sub>n</sub>...Au<sub>n+1</sub> distances change little, see footnote a in Table IV.

The reaction path for Scheme I was approximated by the "linear synchronous transit" method.<sup>20</sup> The pseudorotation barriers in Figure 2 are seen to be quite low, allowing for easy distortions.

**Heats of Formation.** Could these naked clusters be made? The heats of formation were estimated (without zero-point-energy corrections) from

$$\Delta H_f^\circ(\text{EAu}_4^+) = E_{\text{calc}}(\text{EAu}_4^+) - 2E_{\text{calc}}(\text{Au}_2) - \frac{1}{2}E_{\text{calc}}(\text{E}_2) + 2\Delta H_f^{\text{exp}}(\text{Au}_2) + \frac{1}{2}\Delta H_f^{\text{exp}}(\text{E}_2) \quad (1)$$

The results are given in Table V. They are clearly below the E<sup>+</sup> + 2Au<sub>2</sub> dissociation limit. Hence these EAu<sub>4</sub><sup>+</sup> clusters could exist in the gas phase. The X<sup>1</sup>A<sub>1</sub> ground state of Au<sub>4</sub> is a rhombus,<sup>21</sup> which could directly react with E<sup>+</sup>, E = N-As.

The E-Au bond strengths can be estimated from the experimental E<sup>+</sup> + 2Au<sub>2</sub> and the calculated EAu<sub>4</sub><sup>+</sup> energies. The results are 261, 214, and 187 kJ/mol for E = N, P and As, respectively. These numbers are comparable with the D<sub>e</sub> of Au<sub>2</sub> of 221 kJ/mol.

### Clusters with Phosphines, E(AuPH<sub>3</sub>)<sub>4</sub><sup>+</sup>

**Geometries.** The optimized geometries are given in Table II and the corresponding relative energies in Table III.

As seen from Table III, for N(AuPH<sub>3</sub>)<sub>4</sub><sup>+</sup> (1a) the T<sub>d</sub> geometry is preferred, both at HF and MP2 levels, if the phosphine ligands

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Scheme I

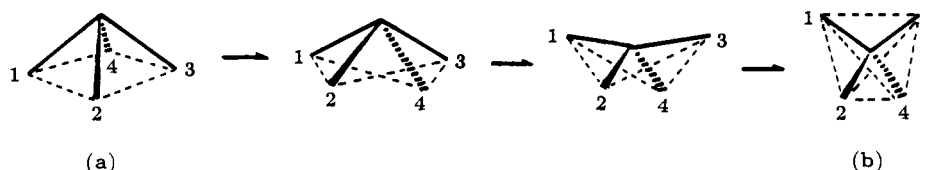


Table IV. MP2-Level Vibrational Frequencies for 2

species	method	geo- metry	frequencies
2a	HF	$T_d$	31 (e), 35 ( $t_2$ ), 141 ( $a_1$ ), 591 ( $t_2$ )
	MP2	$C_{2v}$	22 ( $a_1$ ), 60 ( $a_1$ ), 76 ( $b_1$ ), 89 ( $a_2$ ), 101 ( $b_2$ ), 106 ( $a_1$ ), 404 ( $b_2$ ), 474 ( $b_1$ ), 551 ( $a_1$ )
2b	HF	$T_d$	33 (e), 36 ( $t_2$ ), 113 ( $a_1$ ), 357 ( $t_2$ )
	MP2	$C_{2v}$ <sup>a</sup>	7 ( $a_1$ ), 70 ( $a_1$ ), 84 ( $b_2$ ), 93 ( $b_1$ ), 95 ( $a_2$ ), 106 ( $a_1$ ), 251 ( $b_1$ ), 256 ( $b_2$ ), 318 ( $a_1$ )
2c	HF	$T_d$	33 (e), 35 ( $t_2$ ), 110 ( $a_2$ ), 240 ( $t_2$ )
	HF	$C_{4v}$	21 ( $b_2$ ), 58 (e), 66 ( $b_1$ ), 81 (e), 186 (e), 212 ( $a_1$ )
	MP2	$C_{4v}$	20 ( $b_2$ ), 73 (e), 75 ( $b_2$ ), 81 ( $b_1$ ), 91 ( $a_1$ ), 181 (e), 220 ( $a_1$ )

<sup>a</sup> P–Au1 = 257.1 pm, P–Au2 = 254.3 pm, Au1–P–Au2 = 69.15°, Au1...Au2 = 290.2 pm, diagonal Au1...Au3 = 423.7 pm, and diagonal Au2...Au4 = 395.6 pm. Total energies:  $C_{4v}$ , -140.132875;  $C_{2v}$ , -140.132895.

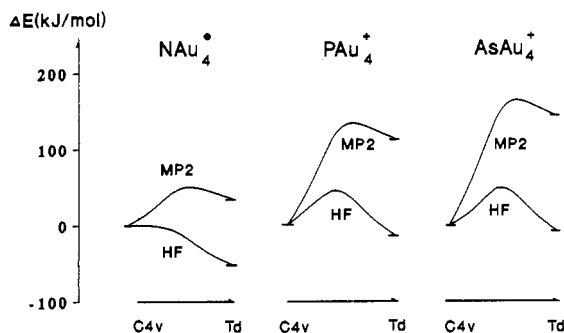


Figure 2. Pseudorotation barriers for 2.

Table V. Heats of Formation (kJ/mol)<sup>a</sup>

system	method	$\Delta H_f$
N <sup>+</sup> + 2Au <sub>2</sub>	expt <sup>b</sup>	2895
	NAu <sub>4</sub> <sup>+</sup>	HF <sup>c</sup>
P <sup>+</sup> + 2Au <sub>2</sub>	expt	2395
	PAu <sub>4</sub> <sup>+</sup>	HF <sup>c</sup>
As <sup>+</sup> + 2Au <sub>2</sub>	expt	2270
	AsAu <sub>4</sub> <sup>+</sup>	HF <sup>d</sup>
N(AuPH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	MP2 <sup>d</sup>	1391
	HF <sup>c</sup>	1371
P(AuPH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	MP2 <sup>c</sup>	1051
	HF <sup>c</sup>	1061
As(AuPH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	MP2 <sup>d</sup>	868
	HF <sup>c</sup>	1090
	MP2 <sup>d</sup>	878

<sup>a</sup> The lower-energy conformations are chosen. The results show that the naked EAu<sub>4</sub><sup>+</sup> species are stable in the gas phase, even including the differences in  $IP_1$  between N, P, As, and Au<sub>2</sub> (1402.3, 1011.7, 946.5, and 888 (20) kJ/mol, respectively).<sup>b</sup> References 24 and 25. <sup>c</sup>  $T_d$  geometry. <sup>d</sup>  $C_{4v}$  geometry.

are included. The calculated MP2 N–Au distance is 213.2 pm. The experimental, distorted  $T_d$  values are  $3 \times 200.5(9)$  and  $1 \times 205(3)$  pm.<sup>1</sup> The corresponding calculated Au–Au distance is 348 pm, slightly above the typical “aurophilic” secondary bond lengths.

The experimental structure of N(AuPR<sub>3</sub>)<sub>4</sub><sup>+</sup> is a distorted  $T_d$  structure of  $C_{3v}$  symmetry, suggesting a very small force constant for this mode. The calculated, MP2  $\partial^2 E / \partial \alpha^2$  ( $\alpha = \text{Au}_{ax} - \text{N} - \text{Au}$ )

values are only 0.00025 and 0.0010 au for NAu<sub>4</sub><sup>+</sup> and N(AuPH<sub>3</sub>)<sub>4</sub><sup>+</sup>, respectively.

For As(AuPH<sub>3</sub>)<sub>4</sub><sup>+</sup> (1c) at the MP2 level, the  $C_{4v}$  geometry is preferred by 71.8 or 132.3 kJ/mol without and with polarization functions, respectively. The As–Au bond length is 260.9 pm (experimental 250 pm), and the Au–As–Au angle is 69.1 (70.7)°. The corresponding Au–Au distance is only 296 (290) pm, at the low end of the “aurophilic” bond range. At HF level a  $T_d$  geometry would be preferred by 40.2 kJ/mol, again corresponding to the idea of dominant correlation effects. The total correlation contribution to the  $C_{4v}$ – $T_d$  energy difference of 71.8 – (–40.2) = 112 kJ/mol is about 4 times the typical aurophilic attraction energy of 30 kJ/mol, due to the four (short) Au...Au interactions.

If one d and f polarization function is added for As(AuPH<sub>3</sub>)<sub>4</sub><sup>+</sup> at the same HF and MP2 geometries, the correlation contribution increases from 112 to 171 kJ/mol. For the (ClAuPH<sub>3</sub>)<sub>2</sub> dimer, counterpoise correction for the basis-set superposition error (BSSE) diminished the Au...Au interaction by roughly a factor of 2.<sup>11</sup> While the BSSE can be estimated in the intermolecular case using a counterpoise correction, it is not obvious how to handle an intramolecular case. An analogous, “internal BSSE” has recently been considered for special conformations of  $C_4$  molecules.<sup>22,23</sup>

For this  $C_{4v}$  hybridization and geometry the Au–As–Au angle only decreases 4.4° from HF to MP2. In the  $C_{2v}$  Se(AuPH<sub>3</sub>)<sub>2</sub> with two Au atoms and one Au...Au bond, this correlation effect was much larger, 16° with the present 11 valence-electron pseudopotential and 22.4° with a 19 valence-electron pseudopotential, including a d and f polarization function.<sup>11</sup>

As expected by Schmidbaur<sup>1</sup> for the so far unknown P(AuPH<sub>3</sub>)<sub>4</sub><sup>+</sup>  $C_{4v}$  geometry is preferred, by 38.7 kJ/mol, half the amount for E = As. The calculated P–Au distance is 246.4 pm and corresponding Au–Au 287 pm.

For E(AuPH<sub>3</sub>)<sub>4</sub><sup>+</sup> systems, it is beyond our computer resources to calculate the vibrational frequencies for the optimized  $C_{4v}$  and  $T_d$  geometries. The  $C_{4v}$  to  $C_{2v}$  distortion, similar to EAu<sub>4</sub><sup>+</sup> case, was checked for As(AuPH<sub>3</sub>)<sub>4</sub><sup>+</sup> ( $C_{4v}$ ) at MP2 level. None was found.

**Phosphines and Thermochemistry.** The effect of the phosphine ligands on the E–Au bond length is a slight shortening by 3–10 pm for each symmetry. The  $C_{4v}$  Au–E–Au angle is increased by 2–7°. The phosphines are however essential in keeping the E = N case tetrahedral. For E = P and As, the  $C_{4v}$  symmetry is favored also without phosphines. For the three cases E = N–As at MP2 level, the phosphines raise the  $C_{4v}$  case with respect to  $T_d$  by 86, 75, and 72 kJ/mol, respectively. For E = P and As it still remains the lower one.

The heats of formation

$$\Delta H_f^\circ(E(\text{AuPH}_3)_4^+) = E_{\text{calc}}(E(\text{AuPH}_3)_4^+) - 2E_{\text{calc}}(\text{Au}_2) - \frac{1}{2}E_{\text{calc}}(\text{E}_2) - 4E_{\text{calc}}(\text{PH}_3) + 2\Delta H_f^{\text{exp}}(\text{Au}_2) + \frac{1}{2}\Delta H_f^{\text{exp}}(\text{E}_2) + 4\Delta H_f^{\text{exp}}(\text{PH}_3) \quad (2)$$

are given in Table V. While the experimental  $\Delta H_f^\circ(\text{PH}_3)$  is only 13.4 kJ/mol,<sup>24</sup> the four phosphines increase the stability of 2a–c

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**Table VI.** Mulliken Population of EAu<sub>4</sub><sup>+</sup> and E(AuPH<sub>3</sub>)<sub>4</sub><sup>+</sup> for "Basis 1" and the "Partially Optimized" HF and MP2 Geometries

system	sym	method	Au s	Au p	Au d	Au	E	PH <sub>3</sub>
NAu <sub>4</sub> <sup>+</sup>	T <sub>d</sub>	HF	0.52	0.12	9.87	+0.49	-0.95	
		MP2	0.65	0.14	9.83	+0.38	-0.52	
PAu <sub>4</sub> <sup>+</sup>	C <sub>4v</sub>	HF	0.56	0.16	9.89	+0.40	-0.59	
		MP2	0.67	0.19	9.84	+0.30	-0.21	
AsAu <sub>4</sub> <sup>+</sup>	T <sub>d</sub>	HF	0.68	0.14	9.93	+0.25	+0.02	
		MP2	0.78	0.15	9.88	+0.19	+0.23	
AsAu <sub>4</sub> <sup>+</sup>	C <sub>4v</sub>	HF	0.69	0.21	9.94	+0.16	+0.37	
		MP2	0.78	0.24	9.86	+0.12	+0.53	
N(AuPH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	T <sub>d</sub>	HF	0.72	0.14	9.94	+0.19	+0.22	
		MP2	0.82	0.15	9.89	+0.15	+0.40	
N(AuPH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	C <sub>4v</sub>	HF	0.71	0.21	9.94	+0.14	+0.45	
		MP2	0.80	0.23	9.87	+0.10	+0.59	
P(AuPH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	T <sub>d</sub>	HF	0.75	0.33	9.76	+0.16	-1.03	+0.34
		MP2	0.87	0.41	9.71	+0.01	-0.59	+0.39
P(AuPH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	C <sub>4v</sub>	HF	0.70	0.37	9.79	+0.14	-0.94	+0.34
		MP2	0.83	0.47	9.74	-0.04	-0.40	+0.39
As(AuPH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	T <sub>d</sub>	HF	0.85	0.37	9.86	-0.08	+0.03	+0.32
		MP2	0.95	0.43	9.80	-0.18	+0.25	+0.37
As(AuPH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	C <sub>4v</sub>	HF	0.82	0.46	9.86	-0.14	+0.25	+0.33
		MP2	0.89	0.57	9.79	-0.24	+0.50	+0.37
As(AuPH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	T <sub>d</sub>	HF	0.88	0.39	9.85	-0.12	+0.19	+0.32
		MP2	0.97	0.44	9.80	-0.21	+0.37	+0.37
As(AuPH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	C <sub>4v</sub>	HF	0.83	0.46	9.86	-0.14	+0.26	+0.33
		MP2	0.88	0.56	9.78	-0.22	+0.44	+0.36

**Table VII.** E–Au, Au–Au, and Au–P(PH<sub>3</sub>) Bond Orders for EAu<sub>4</sub><sup>+</sup> and E(AuPH<sub>3</sub>)<sub>4</sub><sup>+</sup>

system	sym	E–Au		Au–Au		Au–P	
		HF	MP2	HF	MP2	HF	MP2
NAu <sub>4</sub> <sup>+</sup>	T <sub>d</sub>	0.22	0.21	-0.04	-0.08		
	C <sub>4v</sub>	0.16	0.14	0.06	-0.02		
PAu <sub>4</sub> <sup>+</sup>	T <sub>d</sub>	0.34	0.27	-0.05	-0.08		
	C <sub>4v</sub>	0.19	0.11	0.09	-0.01		
AsAu <sub>4</sub> <sup>+</sup>	T <sub>d</sub>	0.34	0.26	-0.05	-0.08		
	C <sub>4v</sub>	0.20	0.14	0.09	0.00		
N(AuPH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	T <sub>d</sub>	0.23	0.20	-0.03	-0.09	0.29	0.18
	C <sub>4v</sub>	0.21	0.16	0.01	-0.06	0.27	0.16
P(AuPH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	T <sub>d</sub>	0.36	0.27	-0.03	-0.07	0.23	0.15
	C <sub>4v</sub>	0.27	0.17	0.06	-0.04	0.21	0.11
As(AuPH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	T <sub>d</sub>	0.37	0.26	-0.03	-0.06	0.22	0.14
	C <sub>4v</sub>	0.27	0.19	0.07	-0.03	0.21	0.11

by 664, 538, and 513 kJ/mol (at the MP2 level for the lowest energy conformation). This can be compared with the MP2 level strengthening of the single, covalent Au–Au bond in H<sub>3</sub>P–Au–Au–PH<sub>3</sub> by 120.8 kJ/mol.<sup>26</sup>

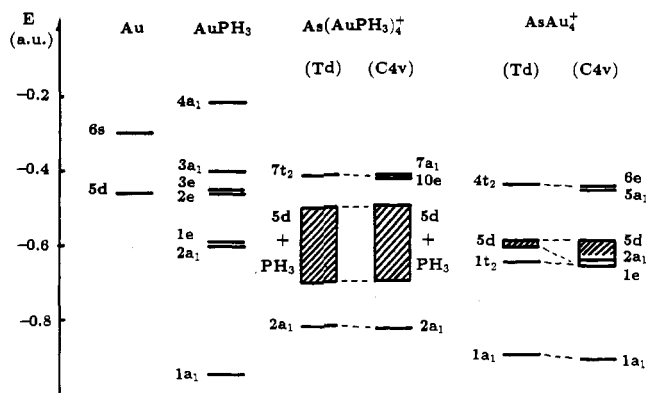
As for the more ionic AuCl, using basis 3 at the MP2 level, the Au–Cl bond length becomes 225.0 pm and  $E_T$  is -594.75152 au. The free PH<sub>3</sub> P–H bond is 143.0 pm, z–P–H angle is 122.8°, and  $E_T$  is -8.17086 au. As the ClAuPH<sub>3</sub>  $E_T$  is -603.02110 au, the phosphine lowers the total energy by 259 kJ/mol.

## Bonding

**Hybridization.** The 6s valence orbital of gold can hybridize with the filled 5d or the empty 6p one. In two-coordinated Au(I)L<sub>2</sub> complexes,<sup>27</sup> the 5d hole dominates for small electronegative ligands while the 6p population dominates for large, electropositive ligands. For the diphosphine, Au(PH<sub>3</sub>)<sub>2</sub><sup>+</sup>, the populations 10- $n_{5d}$  and  $n_{6p}$  are comparable.

The Mulliken populations of the present species are given in Table VI. For the C<sub>4v</sub> E(AuPH<sub>3</sub>)<sub>4</sub><sup>+</sup> at MP2 level, the  $n_{6p}$  values are over 2 times larger than the 5d hole populations. At HF level both quantities are slightly smaller. Correlation effects strongly increase the 5d-to-(6s + 6p) population transfer. They also transfer electrons from the central atom E to the Au atoms.

The bond orders are given in Table VII. There is evident radial, E–Au, and Au–PH<sub>3</sub> bonding. The C<sub>4v</sub> Au–Au bond orders

**Figure 3.** HF Orbital energies of Au, AuPH<sub>3</sub>, As(AuPH<sub>3</sub>)<sub>4</sub><sup>+</sup> (T<sub>d</sub> and C<sub>4v</sub>), and AsAu<sub>4</sub><sup>+</sup> (T<sub>d</sub> and C<sub>4v</sub>).

are small and become negative at MP2 level, suggesting lack of covalent gold–gold bonding, even when the phosphines are added.

The phosphine ligand effects on the EAu<sub>4</sub><sup>+</sup> (T<sub>d</sub>) bond orders are small. The phosphine increases the Au 6s and 6p populations and increases the 5d hole, indicating stronger spd-mixing, as suggested by Rösch *et al.*<sup>6,7</sup>

The C<sub>4v</sub> E–Au bond orders for both naked and "dressed" clusters are positive but smaller than in T<sub>d</sub>.

For E(AuPH<sub>3</sub>)<sub>4</sub><sup>+</sup> (C<sub>4v</sub>) at HF level, the Au–Au bond order is +0.063 and +0.067 for E = P and As, respectively. At MP2 level these numbers become -0.041 and -0.028, but at the same time the "aurophilic" attraction appears. Possibly this could be interpreted as covalent bonding at HF level and a correlation interaction at MP2 level.

**Orbital Energies.** The QR HF orbital energies of Au, AuPH<sub>3</sub>, and the arsenic species are shown in Figure 3. The singly occupied a<sub>1</sub> orbital (SOMO) of AuPH<sub>3</sub> is 6s<sup>0.766</sup>p<sup>0.165</sup>5d<sup>0.003</sup>3p<sup>0.023</sup>p<sup>0.051</sup>s<sup>0.01</sup>. It is oriented away from P. The four such lobe orbitals in As(AuPH<sub>3</sub>)<sub>4</sub><sup>+</sup> (T<sub>d</sub>) span the a<sub>1</sub> and t<sub>2</sub> orbitals in Figure 3, in analogy with the expectations of Scherbaum *et al.*<sup>28</sup> for the octahedral C(AuL)<sub>6</sub><sup>2+</sup>. The latter case was termed a "7-center–8-electron bond" in ref 8. Most of the 5d character of Au remains in the Au+PH<sub>3</sub> "box" in Figure 3. The C<sub>4v</sub> orbital energies are surprisingly similar to the T<sub>d</sub> ones. No Walsh-type behavior can be discerned.

Without the phosphine ligands, in the right-hand part of Figure 3, the naked T<sub>d</sub> cluster forms two bonding t<sub>2</sub> MOs, the lower to Au 5d and the higher to Au 6s. The effect of the phosphine is qualitatively to direct the 5d character toward P, leaving mainly the 6s to bond to the central atom. For naked AsAu<sub>4</sub><sup>+</sup> also the C<sub>4v</sub> orbital energies are quite similar; the 5d band broadens due to the shorter Au–Au distance. The pictures for E = N and P are qualitatively similar.

The Mulliken population analysis shows that the AsAu<sub>4</sub><sup>+</sup> 5a<sub>1</sub> and 6e are bonding orbitals between As 4p and Au (37% Au 6s character). The 2a<sub>1</sub> and 1e have about 90% Au 5d character and only 6.5% As character. Therefore they should be seen as parts of the Au 5d band. If phosphines are added, the highest, 10e and 7a<sub>1</sub> MOs get even more As 4p character while the Au character has more 6s–6p hybridization and even less 5d. The 2a<sub>1</sub>, mainly a As 4s–Au 5d bond, contributes about 1/4th of the total As–Au bond order.

## Conclusion

Our calculations reproduce the experimental T<sub>d</sub> geometry for E(AuPH<sub>3</sub>)<sub>4</sub><sup>+</sup>, E = N (1a), and the C<sub>4v</sub> geometry for E = As (1c). For E = P (1b), a C<sub>4v</sub> structure is predicted, as expected by Schmidbauer.<sup>1</sup> Without the phosphines, for the unknown EAu<sub>4</sub><sup>+</sup>

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(27) See Ref 15, Table V.

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clusters, the correlation contribution to the  $E(C_{4v}) - E(T_d)$  difference is even larger than with them.  $EAu_4^+$  would be approximately pyramidal ( $C_{4v}$ ) for E = N, P, and As. For E = N and P, a slight  $C_{2v}$  distortion occurs. The HF-level bond lengths<sup>8</sup> are realistic, however. Correlation and probably relativity are required to obtain the  $C_{4v}$  structures for **1b** and **1c**. In this sense the Au(I)⋯Au(I) secondary bonds resemble the "correlation-bound" van der Waals complexes, such as Ar<sub>2</sub>, Mg<sub>2</sub>, Ar·HCl or (Cl<sub>2</sub>)<sub>2</sub>.<sup>29</sup> Another bonding analogy is the halogen⋯halogen or S⋯S contacts, as pointed out by Pathaneni and Desiraju<sup>30</sup> in their database analysis of the 693 known Au⋯Au structures. The

present work thus supports our earlier suggestion<sup>10,11</sup> that the "aurophilic" attraction is due to correlation effects. The question is whether the extended Hückel method,<sup>9</sup> in an allegorical sense, includes them.

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