

## Calculated Properties of the 'Empty' $[\text{AuPH}_3]_4^{2+}$ and Related Systems: Role of Covalent and Correlation Contributions

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Quasirelativistic pseudopotential *ab initio* calculations on tetrahedral  $(\text{AuPH}_3)_4^{2+}$  reproduce the experimental Au–Au distance in  $[\text{AuP}(\text{Bu})_3]_4^{2+}$  and suggest that covalent and correlation bonding in this two-electron, four-centre system are comparable.

The possibility of *n*-centre-2-electron(*nc*-2e) systems  $(\text{ML})_n^{(n-2)+}$  (*n* = 3–7, M = Au, L =  $\text{PH}_3$ ) was pointed out by Mingos.<sup>1</sup> For *n* = 4,  $\text{Ag}_4^{2+}$  in aqueous solution has been observed.<sup>2,3</sup> The *n* = 4 case with M = Li and Na was theoretically discussed<sup>4</sup> while the simplest 4c-2e system, free  $\text{H}_4^{2+}$ , was reported not to have local minima.<sup>5</sup> Inelastic neutron scattering evidence exists for a tetrahedral  $(\text{H}_4)^{x+}$  entity with H–H = 80 pm in  $\text{Mn}^{4+}$  vacancies in  $\gamma\text{-MnO}_2$ .<sup>6</sup>

As Zeller *et al.*<sup>7</sup> have prepared the  $[\text{AuPR}_3]_4^{2+}$  ion (R = Bu<sup>t</sup>) in stable compounds, we consider here the nature of bonding in the naked  $\text{M}_4^{2+}$  (M = Ag, Au) and in the  $[\text{AuPH}_3]_4^{2+}$  model system. One question is the relative importance of covalent character<sup>8</sup> and the 'aurophilic' attraction, identified as a correlation effect.<sup>9–11</sup> Both contributions are strongly strengthened by relativity<sup>8–10</sup> and by the phosphines.<sup>8,11</sup> replacing the R(=Me, Ph) in  $\text{PR}_3$  by R = H is acceptable for the geometry but is less acceptable for the energetics.<sup>12</sup>

For both M = Ag and M = Au 19-valence-electron (19VE) quasirelativistic pseudopotentials<sup>13</sup> with corresponding basis sets and GAUSSIAN92 at Hartree–Fock (HF) or second-order Møller–Plesset (MP2) level were used. The calculated  $E_T$  for the naked  $\text{M}_2$ ,  $\text{M}_3^+$  and  $\text{M}_4^{2+}$  (M = Ag, Au) are compared in Fig. 1. The gas-phase reaction  $2\text{M}_2^+ \rightarrow \text{M}_4^{2+}$  is seen to be exothermic for both M = Ag and M = Au, as experimentally found for M = Ag in water.<sup>3</sup> Similarly, the gas-phase reactions  $2\text{M}^+ + \text{M}_2 \rightarrow \text{M}_4^{2+}$  are calculated to be exothermic.

The bond distances are given in Table 1. The importance of the correlation effect on  $R_e$  increases with *n*. This is expected, as  $\text{M}_4^{2+}$  has six Au–Au pairs, each with a van der Waals interaction, but only one electron pair, leading to a covalent bond order of 1/6. Note that gold atoms are smaller than silver, the Ag > Au difference increasing with *n*. A relativistic multiple-scattering (MS) analysis of the bonding in the naked

**Table 1** Calculated M–M distances,  $R_e$  (in pm).  $D_{3h}$  symmetry assumed for  $\text{M}_3^+$ ,  $T_d$  symmetry assumed for  $\text{M}_4^{2+}$  and  $(\text{ML})_4^{2+}$ , L =  $\text{PH}_3$

M	Method	Species			
		$\text{M}_2$	$\text{M}_3^+$	$\text{M}_4^{2+}$	$(\text{ML})_4^{2+}$
Ag	HF	271.1	287.8	310.2	—
	MP2	259.0	271.6	284.8	—
	Exp.	253.0	—	—	—
Au	HF	262.8	277.4	292.0	289.9 <sup>a</sup>
	MP2	252.3	263.4 <sup>b</sup>	272.3	271.8 <sup>c</sup>
	Exp.	249.2	—	—	270.3–273.0 <sup>d</sup>

<sup>a</sup> Au–P optimized to 246.0 pm. P–H and Au–P–H assumed to be 143.0 pm and 119.4°, respectively. <sup>b</sup> The calculated MP2 frequencies  $\nu(a'_1)$  and  $\nu_2(e')$  and 187 and 123  $\text{cm}^{-1}$ , respectively (H–P–H = 98.0°).

<sup>c</sup> Experimental Au–P = 230.5 pm (ref. 7). <sup>d</sup> Ref. 7.

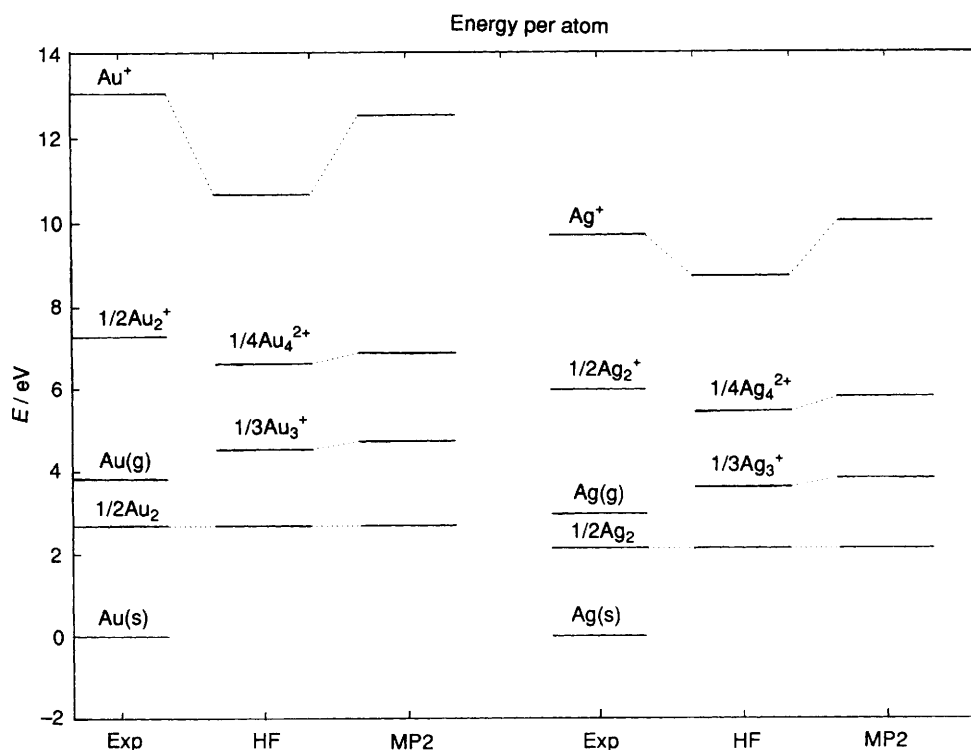


Fig. 1 Heats of formation per atom (in eV) compared with that of M(s). The theoretical scales are fixed to the experimental scale for M<sub>2</sub>(g).

**Table 2** Energy lowering,  $\Delta E$ , (in kJ mol<sup>-1</sup>) for the reactions  $\text{NAu}_4^+ + 4 \text{PH}_3 \rightarrow \text{N}(\text{AuPH}_3)_4^+$  (ref. 11) and  $\text{Au}_4^{2+} + 4 \text{PH}_3 \rightarrow (\text{AuPH}_3)_4^{2+}$  (present work), and  $\text{Au}_2 + 2 \text{PH}_3 \rightarrow (\text{AuPH}_3)_2$  (ref. 8).

Species	$\Delta E$	
	HF	MP2
$\text{NAu}_4^+$	-480	-664
$\text{Au}_4^{2+}$	-735	-1220
$\text{Au}_2$	-86.3	-120.8

$\text{Au}_4^{2+}$  suggests the total atomic populations  $6s^{0.64}6p^{0.23}5d^{9.63}$  at each  $\text{Au}^{0.5+}$ .<sup>14</sup> We find at HF-level the Mulliken populations  $6s^{0.59}6p^{0.02}5d^{9.88}5f^{0.02}$ . A natural-orbital population analysis gives  $6s^{0.49}6p^{0.04}5d^{9.97}$ . The Mulliken population analysis gives an Au–Au overlap population of 0.054. the bonding  $a_1$  MO is the HOMO, in the HF model, while it was embedded in the 5d band in the MS model.<sup>14</sup>

Already without phosphines, the MP2  $\text{Au}_4^{2+}$  bond length of 272.3 pm agrees with the experimental (ML) $_4^{2+}$  one of 270.3–273.0 pm. At the HF level, the influence of the phosphine on the Au–Au distance is small. An MP2 optimization for  $(\text{AuPH}_3)_4^{2+}$  indeed gives an almost unchanged Au–Au distance of 271.8 pm. The MP2  $a_1$  stretching force constant is  $5.8 (10^2 \text{ N m}^{-1} = 1 \text{ mdyn } \text{\AA}^{-1})$ .

The energy lowering due to phosphines is given in Table 2. As seen, it is larger for the present, 'empty' cluster than for the nitrogen-centred one.

We conclude that the experimental Au–Au distance of the 'empty' cluster  $(\text{AuL})_4^{2+}$  is reproduced by theory. Both covalency and correlation effects contribute to its stability. The largest calculated correlation contributions per Au<sup>I</sup>–Au<sup>I</sup> pair in various  $(\text{XAuPH}_3)_2$  dimers were up to 25 kJ mol<sup>-1</sup>,<sup>15</sup> or ca. 150 kJ mol<sup>-1</sup> for six pairs. The total bonding energy per valence electron pair is 225 and 366 kJ mol<sup>-1</sup> for diatomic and metallic gold, respectively. Hence, the two contributions in the present case are expected to be comparable.

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