Calculated Properties of the 'Empty' $[AuPH_3]_4^{2+}$ and Related Systems: Role of Covalent and Correlation Contributions

Pekka Pyykkö* and Nino Runeberg

Department of Chemistry, University of Helsinki, PO Box 19 (Et. Hesperiankatu 4), 00014 Helsinki, Finland

Quasirelativistic pseudopotential *ab initio* calculations on tetrahedral $(AuPH_3)_4^{2+}$ reproduce the experimental Au–Au distance in $[AuP(Bu^t)_3]_4^{2+}$ and suggest that covalent and correlation bonding in this two-electron, four-centre system are comparable.

The possibility of *n*-centre-2-electron(*n*c-2e) systems $(ML)_n^{(n-2)+}$ (n = 3–7, M = Au, L = PH_3) was pointed out by Mingos.[1] For n = 4, Ag_4^{2+} in aqueous solution has been observed.[2,3] The n = 4 case with M = Li and Na was theoretically discussed[4] while the simplest 4c-2e system, free H_4^{2+}, was reported not to have local minima.[5] Inelastic neutron scattering evidence exists for a tetrahedral $(H_4)^{x+}$ entity with H–H = 80 pm in Mn^{4+} vacancies in γ-MnO_2.[6]

As Zeller *et al.*[7] have prepared the $[AuPR_3]_4^{2+}$ ion (R = Bu^t) in stable compounds, we consider here the nature of bonding in the naked M_4^{2+} (M = Ag, Au) and in the $[AuPH_3]_4^{2+}$ model system. One question is the relative importance of covalent character[8] and the 'aurophilic' attraction, identified as a correlation effect.[9–11] Both contributions are strongly strengthened by relativity[8–10] and by the phosphines.[8,11] replacing the R(=Me, Ph) in PR_3 by R = H is acceptable for the geometry but is less acceptable for the energetics.[12]

For both M = Ag and M = Au 19-valence-electron (19VE) quasirelativistic pseudopotentials[13] 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 M_2, M_3^+ and M_4^{2+} (M = Ag, Au) are compared in Fig. 1. The gas-phase reaction 2 $M_2^+ \rightarrow M_4^{2+}$ is seen to be exothermic for both M = Ag and M = Au, as experimentally found for M = Ag in water.[3] Similarily, the gas-phase reactions $2M^+ + M_2 \rightarrow M_4^{2+}$ 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 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 M_3^+, T_d symmetry assumed for M_4^{2+} and $(ML)_4^{2+}$, L = PH_3

		Species			
M	Method	M_2	M_3^+	M_4^{2+}	$(ML)_4^{2+}$
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[a]
	MP2	252.3	263.4[b]	272.3	271.8[c]
	Exp.	249.2	—	—	270.3-273.0[d]

[a] Au–P optimized to 246.0 pm. P–H and Au–P–H assumed to be 143.0 pm and 119.4°, respectively. [b] The calculated MP2 frequencies $\nu(a'_1)$ and $\nu_2(e')$ and 187 and 123 cm^{-1}, respectively (H–P–H = 98.0°). [c] Experimental Au–P = 230.5 pm (ref. 7). [d] Ref. 7.

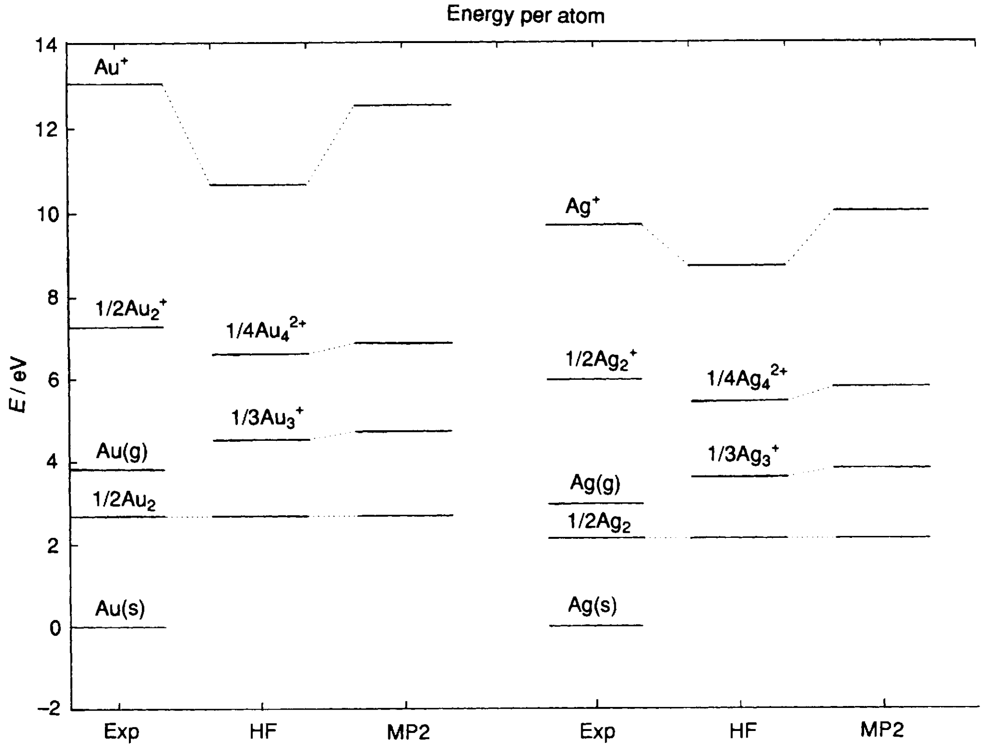

Fig. 1 Heats of formation per atom (in eV) compared with that of M(s). The theoretical scales are fixed to the experimental scale for $M_2(g)$.

Table 2 Energy lowering, ΔE, (in kJ mol^{-1}) for the reactions $NAu_4^+ + 4\ PH_3 \rightarrow N(AuPH_3)_4^+$ (ref. 11) and $Au_4^{2+} + 4\ PH_3 \rightarrow (AuPH_3)_4^{2+}$ (present work), and $Au_2 + 2\ PH_3 \rightarrow (AuPH_3)_2$ (ref. 8).

	ΔE	
Species	HF	MP2
NAu_4^+	−480	−664
Au_4^{2+}	−735	−1220
Au_2	−86.3	−120.8

Au_4^{2+} suggests the total atomic populations $6s^{0.646}6p^{0.235}5d^{9.63}$ at each $Au^{0.5+}$.[14] We find at HF-level the Mulliken populations $6s^{0.596}6p^{0.025}5d^{9.885}f^{0.02}$. A natural-orbital population analysis gives $6s^{0.496}6p^{0.045}5d^{9.97}$. 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.[14]

Already without phosphines, the MP2 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 $(AuPH_3)_4^{2+}$ indeed gives an almost unchanged Au–Au distance of 271.8 pm. The MP2 a_1 stretching force constant is 5.8 (10^2 N m^{-1} = 1 mdyn Å^{-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 $(AuL)_4^{2+}$ is reproduced by theory. Both covalency and correlation effects contribute to its stability. The largest calculated correlation contributions per Au^I–Au^I pair in various $(XAuPH_3)_2$ dimers were up to 25 kJ mol^{-1},[15] or *ca.* 150 kJ mol^{-1} for six pairs. The total bonding energy per valence electron pair is 225 and 366 kJ mol^{-1} for diatomic and metallic gold, respectively. Hence, the two contributions in the present case are expected to be comparable.

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References

1 D. G. Evans and D. M. P. Mingos, *J. Organomet. Chem.*, 1985, **295**, 389.
2 R. Tausch-Treml, A. Henglein and J. Lilie, *Ber. Bunsenges. Phys. Chem.*, 1978, **82**, 1335.
3 B. G. Ershov, E. Janata, A. Henglein and A. Fojtik, *J. Phys. Chem.*, 1993, **97**, 4589.
4 M. N. Glukhovtsev, P.v.R. Schleyer and A. Stein, *J. Phys. Chem.*, 1993, **97**, 5541.
5 M. N. Glukhovtsev, P.v.R. Schleyer and K. Lammertsma, *Chem. Phys. Lett.*, 1993, **209**, 207.
6 F. Fillaux, H. Ouboumour, C. Cachet, J. Tomkinson, G. J. Kearley and L. T. Yu, *Chem. Phys.*, 1992, **164**, 311.
7 E. Zeller, H. Beruda and H. Schmidbaur, *Inorg. Chem.*, 1993, **32**, 3203.
8 P. Schwerdtfeger and P. D. W. Boyd, *Inorg. Chem.*, 1992, **31**, 327.
9 P. Pyykkö and Y.-F. Zhao, *Angew. Chem.*, 1991, **103**, 622; *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 604.
10 J. Li and P. Pyykkö, *Chem. Phys. Lett.*, 1992, **197**, 586.
11 J. Li and P. Pyykkö, *Inorg. Chem.*, 1993, **32**, 2630.
12 O. D. Häberlen and N. Rösch, *J. Phys. Chem.*, 1993, **97**, 4970.
13 Ag: D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuss, *Theor. Chim. Acta*, 1990, **77**, 123, (8s7p6d1f)/[6s5p3d1f]. Au: P. Schwerdtfeger, M. Dolg, W. H. E. Schwarz, G. A. Bowmaker and P. D. W. Boyd, *J. Chem. Phys.*, 1989, **91**, 1762, (8s6p5d1f)/[7s3p4d1f]. α_f = 0.20 added to both. P: See ref. 9, (5s5p1d)/[2s2p1d]. H: T. H. Dunning Jr. and P. J. Hay, in *Modern Theoretical Chemistry 3*, Plenum, New York, 1977, pp. 1–28. (4s1p)/[2s1p], α_p = 0.1811.
14 R. Arratia-Perez and G. L. Malli, *J. Chem. Phys.*, 1986, **84**, 5891.
15 P. Pyykkö, J. Li and N. Runeberg, *Chem. Phys. Lett.*, (submitted).