Tetrahedral Gold–Phosphine Clusters: a Relativistic Molecular Orbital Study*

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The recently characterized cluster $[\{Au(PBu^t_3)\}_4]^{2+}$ has been investigated by the quasi-relativistic and relativistic versions of the LCAO-SCF molecular orbital approach at the non-empirical CNDO/1 level. The optimized geometry agrees well with available experimental data. The naked gold cluster alters its properties dramatically when phosphine ligands are added. The simple phosphine PH_3 is a rather poor model of more complex phosphines, like PBu^t_3. The former is not capable of sufficient donation and thus it induces an instability with respect to reduction. The polar environment assists positively in the redox stabilization of the cluster. The effect of the phosphine ligands lies in the saturation of the high electron affinity of the $\{Au_4\}^{2+}$ core and in the population of the d_{z^2} sublevel.

Phosphine ligands of the PR_3 type play a principal role in the stabilization of gold clusters. Simple forms of the $\{Au_n\}$ core polyhedra have been found, for example in $[\{Au(PBu^t_3)\}_4]^{2+}$ (tetrahedron),[1] $[\{Au[P(C_6H_4Me\text{-}p)_3]\}_6]^{2+}$ or $[C(AuPPh_3)_6]^{2+}$ (octahedron)[2,3] and $[Pt(AuPPh_3)_8]^{3+}$ (square antiprism).[4] Evidently, naked clusters cannot be stabilized unless phosphine ligands are present.

Earlier theoretical works on naked $[Au_n]^q$ clusters[5–7] have been overcome recently by more complex calculations for non-centred $[\{Au(PR_3)\}_n]^q$ clusters[8,9] and main-group-element (E) centred $[\{E(AuPR_3)\}_n]^q$ clusters.[10,11] In the above studies the simple phosphine (R = H) has been considered. It was proposed[12] that this is sufficient enough for the geometry (less accurate for the energy properties) of the cluster. However, no gold cluster with PH_3 ligands really exists. Probably PH_3 ligands are not able to saturate the high electron affinity of the $[Au_4]^{2+}$ core and consequently the system is unstable with respect to reduction. This aspect has not been investigated theoretically so far.

Method

In order to verify the above hypothesis approximate LCAO-SCF (linear combination of atomic orbitals-self-consistent field) molecular orbital calculations have been done. A reliable description of actual gold clusters, however, requires the following enlargement of the theoretical approach: (*i*) inclusion of the relativistic corrections just for the gold atom; mass-velocity, Darwin and spin–orbit terms describe the dominant part of the relativistic effects; (*ii*) involvement of more complex phosphines PR_3 with R = Me, Bu^t, Ph and eventually $p\text{-}MeC_6H_4$; (*iii*) inclusion of electron correlation effects; and (*iv*) at least a limited geometry optimization.

Unfortunately all these requirements are difficult to fulfil completely at the present time. Most published theoretical studies comprise scalar-relativistic (quasi-relativistic) calculations which deal with the single-component wavefunction and real orbitals. In these the mass-velocity term and eventually the Darwin term are added to the traditional non-relativistic Hamiltonian. Depending on further simplifications, the more approximate (like quasi-relativistic complete and intermediate neglect of differential overlap, CNDO and INDO) or less approximate (like quasi-relativistic pseudo-potential) methods are applied. As regards the four-component wavefunction, the spin–orbit splitting is naturally involved. This approach, however, is an order of magnitude more time and computer storage consuming since the basis set is doubled (having lower and upper component functions) and the orbitals become complex. Relativistic extended Hückel (REX), relativistic CNDO/1, relativistic multiple-scattering (MS) and relativistic DVM-Xα methods belong to this class.

As the present study concerned several clusters, the biggest represented by $[\{Au(PBu^t_3)\}_4]^{2+}$ **1** having 164 atoms (see Fig. 1), the quasi-relativistic CNDO/1 method[13] and its relativistic (four-component) counterpart[14] (non-empirical versions) were applied which permit the geometry optimization in a reasonable time.[15] The basis set consists of valence orbitals without (BS1) and/or with (BS2) 6p functions at the gold centre, thus yielding 325 molecular orbitals (in the quasi-relativistic approach) and eventually 650 complex spin orbitals (in the relativistic treatment). The ground-state reference electron configuration of $5d^{10}6s^16p^0$ for the gold atom has been used with the

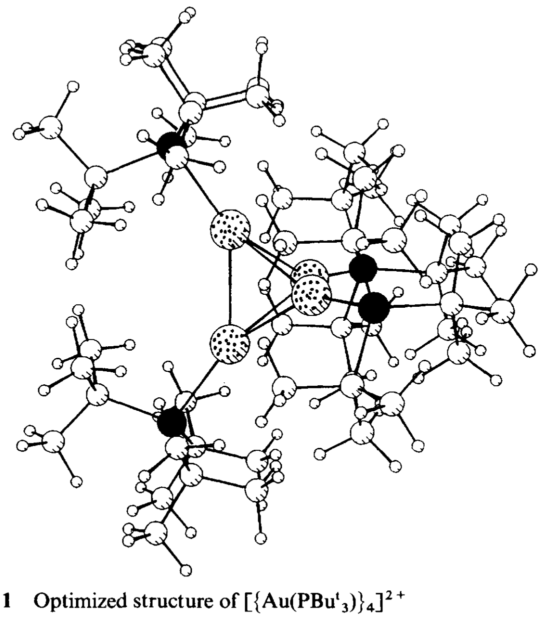

Fig. 1 Optimized structure of $[\{Au(PBu^t_3)\}_4]^{2+}$

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* *Non-SI units employed:* eV ≈ 1.60 × 10^{-19} J, Ry ≈ 2.18 × 10^{-18} J.

Table 1 Calculated distances (pm) in some gold systems

		QR-CNDO/1[a]		R-CNDO/1[b]			
		BS1	BS2	BS1	BS2	Other	Experimental
Au–Au distances							
Au_2		247.1	242.7	247.3	242.6	262.8[c]	247.2
	+MP2	247.4	241.4	247.6	241.5	252.3[c]	
$[Au_4]^{2+}$		269.9	242.6	270.0	243.6	292.0[c]	
	+MP2	270.0	244.4			272.3[c]	
$[\{Au(PH_3)\}_4]^{2+}$		278.5	243.0			289.9[c,d]	
	+MP2	278.8	243.1			271.8[c,d]	
$[\{Au(PMe_3)\}_4]^{2+}$		279.9[d]	243.0[d]				
$[\{Au(PBu^t{}_3)\}_4]^{2+}$		282.3[d]	263.4[d]				270.3–273.0
Au–P distances							
$[AuMe(PH_3)]$		264.3	233.2			229[d,e]	
$[AuMe(PMe_3)]$		264.7	224.3[d]			225[d,e]	228
$[AuMe(PPh_3)]$		338.5	222.0[d]			228[d,e]	227.9

[a] QR = Quasi-relativistic. [b] R = Relativistic. [c] QR-PS = Quasi-relativistic pseudopotential.[9] [d] Some coordinates kept fixed. [e] LDF = Local density functional.[12]

corresponding orbital energies and exponents of Slater-type orbitals generated *via* atomic Dirac–Fock calculations.[16] Since the polarity of an environment may influence some properties of the complex under study, a modified Germer model of solvation[17] (a type of continuous model) was applied for several values of the relative permittivity ε_r.

Table 1 gives information about the reliability of the method used. It is seen that the Au–Au distance is reproduced satisfactorily for the molecule Au_2 and that configuration interaction (MP2 correction) has only a minor effect. Although basis set BS1 is better for Au_2, BS2 is favoured for more complex systems like $[AuMe(PMe_3)]$ and $[AuMe(PPh_3)]$: the calculated Au–P distances are 224 (228) and 220 (228) pm, respectively, the experimental values being given in parentheses. Unless explicitly noted, the results presented below refer to basis set BS2.

Table 2 Results of the geometry optimization by QR-CNDO/1 (BS2)

		$[\{Au(PR_3)\}_4]^{2+}$		
Parameter*	$[Au_4]^{2+}$	R = H	Me	Bu^t
R(Au–Au)	242.6	243.0	243.0	263.4 (270.3–273.0)
R(Au–P)		226.6	222.9	229.7 (230.4–230.6)
R(P–H)		138.9		
θ(Au–P–H)		100.0		
R(P–C)			182.9	186.7
θ(Au–P–C)			[119.0]	103.9 (109)
R(C–C)				151.8
θ(P–C–C)				110.8 (109)
R(C–H)			[108.0]	[108.0]
θ(C–C–H)			[109.0]	[109.0]

* Distances in pm, angles in °. Fixed values in square brackets, experimental data in parentheses.

Results

The geometry of the $[(AuPR_3)_4]^{2+}$ clusters was optimized with respect to several parameters (Table 2), fixed parameters being given in square brackets. The calculated bond lengths for **1** do not differ substantially from the available experimental data (given in parentheses): *R*(Au–Au) = 263.4 (271.6) and *R*(Au–P) = 229.7 (230.5) pm. The Au–Au contacts are definitely longer than in simplified models of $[\{Au(PMe_3)\}_4]^{2+}$, $[\{Au(PH_3)\}_4]^{2+}$ and $[Au_4]^{2+}$ where values of 243.0, 243.0 and 242.6 pm, respectively, have been found.

Recent quasi-relativistic pseudo-potential *ab initio* calculations[9] yielded values of 289.9 pm at the SCF level (*a*) and 271.8 pm after MP2 corrections to electron correlation (*b*) for $[\{Au(PH_3)\}_4]^{2+}$; these values are shorter than those calculated for the naked cluster $[Au_4]^{2+}$ [292.0 (*a*) and 272.3 pm (*b*)]. Evidently such a prediction is chemically unacceptable as the increased electron donation cannot induce a cluster compression. This drawback may originate in too weak a basis set.

The energies of the highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO) (see Table 3) exhibit dramatic changes when passing from the naked cluster $[Au_4]^{2+}$ to a simple phosphine model $[\{Au(PH_3)\}_4]^{2+}$ and to the real structure of $[\{Au(PBu^t{}_3)\}_4]^{2+}$. {A similar effect has been noticed recently for the $[AuMe(PR_3)]$ series, R = H, Me or Ph.}[12] Thus the simple phosphine PH_3 seems to be a poor model for PR_3; R = Bu^t is responsible for the shift of orbital energies to higher (less negative) values. It should be noted that a negative value of the E_{LUMO} can be considered as an indicator of the redox instability;[8] the complex with an extra electron will have a lower value of the total energy in this case and thus it undergoes spontaneous reduction. The $PBu^t{}_3$ ligands make the above tendency less pronounced: the electron affinity (ΔSCF value) drops from 24.7 for $[Au_4]^{2+}$ to 7.8 eV for L = PH_3, 6.5 eV for L = PMe_3 and finally to 3.8 eV for L = $PBu^t{}_3$.

A final stabilization of the LUMO level (*i.e.* its shift towards positive energies) may be obtained when the dielectric properties of the surroundings are considered. Additional SCF calculations for $[\{Au(PBu^t{}_3)\}_4]^{2+}$ using $\varepsilon_r = 10$ or 20 gave shifts of the orbital energies (Table 3). Another SCF calculation for the monocation $[\{Au(PBu_3{}^t)\}_4]^+$ confirmed the above assumption: the electron affinity drops to a value of 1.27 eV.

The phosphine ligands, of course, alter the effective atomic charge on the gold atom, *q*(Au). Within the series of PR_3 = none, PH_3, PMe_3 and $PBu^t{}_3$ the charge decreases from +0.50 to −0.44, −0.50 and −0.59. This manifested also in the lengthening of the Au–Au contacts. Since the N(6p) population is overestimated by the method used (this is a general failure of all-valence calculations), it produces too negative an effective atomic charge on the gold atom. When the 6p orbitals are switched off using the basis set BS1 the negative charges on the gold atoms alter to positive ones. In both cases the trend in atomic charges is conserved.

The bond multiplicity (Wiberg) index *W*(A–B) shows that both the Au–Au and Au–P bonds become weaker with increasing donation from the phosphines. The same effect is seen from the bicentric (interaction) part of the total energy *E*(A–B).

It is difficult to present a complete MO interaction diagram for systems like $[\{Au(PBu^t{}_3)\}_4]$ because of the large number of

Table 3 Energies and atomic charges[a]

		$[\{Au(PR_3)\}_4]^{2+}$				
				Bu^t		
Parameter	$[Au_4]^{2+}$	H	Me	$\varepsilon_r = 1$	10	20
Quasi-relativistic CNDO/1						
ΔSCF	24.71	7.79	6.49	3.80	1.40	1.27
E_{LUMO}	t −22.76	t −7.46	t −6.02	t −3.27	−1.40	−1.29
E_{HOMO}	t −32.60	a −15.97	a −12.83	a −9.14	−6.58	−6.44
q(Au)	0.50	−0.44	−0.50	−0.59	−0.71	−0.72
N(s)	0.67	0.68	0.69	0.74	0.77	0.77
N(p)	0.82	1.19	1.21	1.12	1.17	1.17
N(d)	9.01	9.57	9.60	9.73	9.77	9.77
W(Au–Au)	1.06	0.73	0.73	0.60		
W(Au–P)	—	0.85	0.78	0.65		
E(Au–Au)	−20.1	−19.1	−19.1	−16.6		
E(Au–P)	—	−24.2	−24.0	−20.8		
Relativistic CNDO/1						
E_{LUMO}	e −23.69	e −7.45	q −6.09	q −3.34		
E_{HOMO}	e −31.72	e −16.11	e −13.01	e −9.30		
q(Au)	0.50	−0.43	−0.50	−0.59		
N(s)	0.68	0.68	0.70	0.75		
$N(p_{\frac{1}{2}})$	0.25	0.42	0.43	0.40		
$N(p_{\frac{3}{2}})$	0.58	0.74	0.78	0.73		
$N(d_{\frac{3}{2}})$	3.78	3.89	3.90	3.93		
$N(d_{\frac{5}{2}})$	5.20	5.67	5.69	5.78		
W(Au–Au)	1.06	0.74	0.74	0.60		
W(Au–P)	—	0.86	0.78	0.66		

[a] Energies in eV, charges in units of e. [b] Level degeneracy: a = singly, e = doubly, t = triply, q = quadruply.

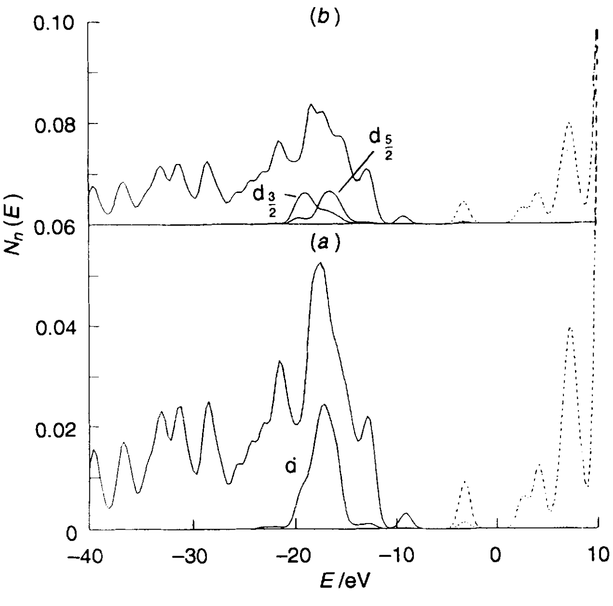

Fig. 2 Density of state functions for $[\{Au(PBu^t_3)\}_4]^{2+}$: (*a*) quasi-relativistic CNDO/1 method, (*b*) relativistic CNDO/1 method

orbitals (325 in this case). A more suitable presentation may be given by the density of states function. This is generated through the formula (1) where σ is a broadening parameter (typically

$$N(E) = (2\pi\sigma)^{-\frac{1}{2}} \sum_i P_i \exp[(E - E_i)^2/2\sigma^2] \qquad (1)$$

0.544 eV = 0.04 Ry), E_i = energy of the ith molecular orbital and P_i is the projection (net orbital population) when the projected density of state functions is generated. The density of states function normalized to the number of basis-set functions, $N_n(E) = N(E)/n_{AO}$, is plotted in Fig. 2 together with its d-orbital projection. The gold d levels are located just below the top of the valence band.

All the above considerations have been reinvestigated in the light of the relativistic (four-component) CNDO/1 calculations. In such an approach the basis set is doubled, yielding 650 complex spin orbitals. Within the T′ double group notation the triply degenerate levels (like LUMO) are split into quadruply (q) and doubly (e) degenerate counterparts, the former capable of occupation by four electrons and the latter by an electron pair. Moreover, as we have lower ($p_{\frac{1}{2}}$, $d_{\frac{3}{2}}$) and upper ($p_{\frac{3}{2}}$, $d_{\frac{5}{2}}$) components of the radial part of the atomic orbitals, they form two sub-bands of molecular orbitals with prevailing $d_{\frac{3}{2}}$ and $d_{\frac{5}{2}}$ projections, respectively (Fig. 2). The total density of states profile, however, alters only slightly when passing from the quasi-relativistic to the relativistic approach.

The values of the atomic charges q(Au) and the spin–orbital populations N(s), $N(p_{\frac{1}{2}})$, $N(p_{\frac{3}{2}})$, $N(d_{\frac{3}{2}})$ and $N(d_{\frac{5}{2}})$ provide a more detailed information about the electron-density distribution. The most significant change is represented by an increase in $N(d_{\frac{5}{2}})$ from 5.20 in $[Au_4]^{2+}$ to 5.67 in $[\{Au(PH_3)\}_4]^{2+}$, 5.69 in $[\{Au(PMe_3)\}_4]^{2+}$ and 5.78 in $[\{Au(PBu_3^t)\}_4]^{2+}$. Thus the more complex phosphine ligands effect the electron donation to the metal $d_{\frac{5}{2}}$ spin orbitals.

The quasi-relativistic pseudo-potential *ab initio* approach, similar to that in ref. 9, has been applied to the $[\{Au(PH_3)\}_4]^{2+}$ cluster [C_1 symmetry, R(Au–Au) = 272.06, R(Au–P) = 246.0 and R(P–H) = 143.0 pm; valence basis set [6s5p3d] for Au, [2s2p] for P and [2s] for H atoms} with the aim of showing that the LUMO still has a negative energy: $E_{LUMO} = -5.90$ eV indicates instability with respect to reduction.

In conclusion it may be pointed out that the naked gold clusters alter their properties dramatically when phosphine ligands are added. The simple phosphine PH_3 is a rather poor model of the more complex phosphines, like PBu^t_3, as it induces instability with respect to reduction.

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