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Role of Phosphine Ligands in Gold Cluster Chemistry. Relativistic SCF Calculations on Au_2 and $Au_2(PH_3)_2$

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The chemistry of gold cluster compounds is still an open and often surprising area.[1] Many of the clusters are unique in structure and in chemical properties,[2] and simple classification rules are not available.[1] The Ph_3PAu fragment (Ph = C_6H_5), proposed as isolobal to the hydrogen radical,[3,4] is well-known to form a variety of clusters with a wide range of different nuclearities, containing for example gold units of the form Au_2, Au_4, or Au_{13}.[5,6] The simplest member of this series, $Au_2(PPh_3)_2$, is claimed[5] to have an unexpected nonlinear P-Au-Au-P conformation possibly due to agostic Au-H(*o*-Ph) interactions. Apart from semiempirical calculations,[4,6-8] there are only few theoretical investigations and only on uncoordinated gold clusters,[9-20] and very little is known about the stability and bonding in such compounds.[6,17] This is mainly due to the very large number of electrons involved in such calculations, which makes SCF calculations very expensive computationally. Furthermore, relativistic effects are most important for understanding the chemistry and physics of gold.[19,21-24] Anomalies, such as the instability of AuF or the increased ionic character of intermetallic gold compounds, can be explained in terms of a relativistic 6s-orbital contraction.[19,24] It would be not surprising if the stability of gold cluster compounds is strongly influenced by relativistic effects.

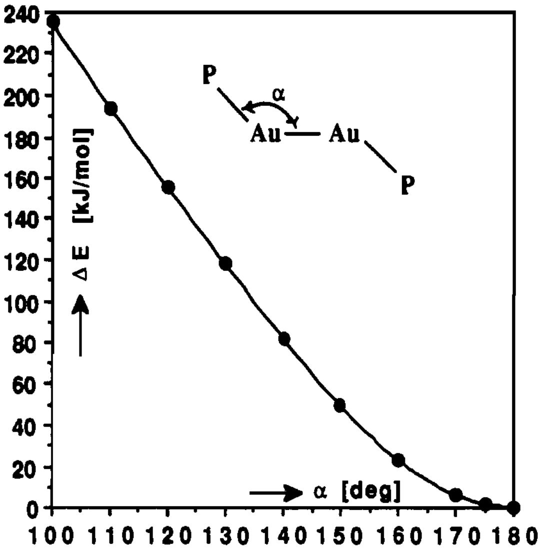
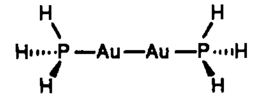


Figure 1. Relativistic MP2 potential curve $\Delta E(\alpha)$ for the P-Au-Au-P trans bending in $Au_2(PH_3)_2$. All other internal coordinates are fixed to the linear P-Au-Au-P arrangement (Table I).

The lack of strong relativistic effects in copper and silver compared to gold (see ref 21) may explain the different chemistry within the group 11 cluster compounds. The d orbitals in copper and silver are assumed to be corelike in contrast to those of gold. Au(5d) and Au(6p) participation in gold cluster formation may be essential for explaining the high stabilities in such systems.[7] However, Malli recently disputed the significance of such contributions in gold chemistry.[25] We discuss this in detail for the smallest known Au cluster, $Au_2(PPh_3)_2$, which we simulate by the dinuclear model species $Au_2(PH_3)_2$ (**1**). We also reinvestigate Au_2 at the nonrelativistic and relativistic level of the theory to study the effects of electron correlation by means of the Møller-Plesset perturbation theory of second order (MP2). The role of the PR_3 ligands is investigated at both the Hartree-Fock (HF) and MP2 level.[26]



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0020-1669/92/1331-0327$03.00/0

Table I. Optimixed Bond Distances r (in Å) and Au-P-H Angles α (in deg) for PH_3, $AuPH_3$, $Au_2(PH_3)_2$, and Au_2[a]

molecule	method	r(Au-P)	r(P-H)	r(Au-Au)	α(Au-P-H)	D_e
PH_3	NRHF		1.421		121.39	
	NRMP2		1.429		123.20	
	exptl		1.420		122.86	
Au_2	NRHF			2.930		28.0
	NRMP2			2.830		105.9
	RHF			2.633		60.7
	RMP2			2.562		182.7
	exptl			2.472		221
$AuPH_3$	NRHF	4.231	1.419		121.89	5.8
	NRMP2	3.037	1.424		121.27	16.9
	RHF	4.240	1.419		121.90	8.3
	RMP2	2.477	1.420		119.72	54.2
$Au_2(PH_3)_2$	NRHF	3.122	1.415	2.926	120.73	62.2
	NRMP2	2.801	1.422	2.823	120.84	164.7
	RHF	2.614	1.411	2.623	119.78	147.0
	RMP2	2.440	1.418	2.550	119.05	303.5

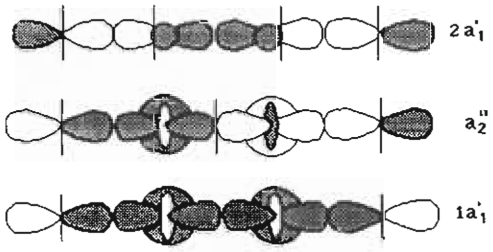
[a] The binding energies D_e (in kJ/mol) are defined as $AuPH_3 \rightarrow Au + PH_3$ for $AuPH_3$ and $Au_2(PH_3)_2 \rightarrow 2AuPH_3$ for $Au_2(PH_3)_2$ (D_e is not corrected for zero-point vibrational contributions). Experimental values for Au_2 and PH_3 were taken from refs 29 and 30.

Table II. Symmetric Stretching Force Constants k_e(Au-X) in mdyn/Å per Au-X Bond (X = Au, P)[a]

		k_e(Au-Au)		k_e(Au-P)	
molecule	method	NR	R	NR	R
Au_2	HF	0.57	1.34		
	MP2	0.78	1.78		
	exptl		2.11		
$AuPH_3$	HF			0.01	0.01
	MP2			0.23	0.68
$Au_2(PH_3)_2$	HF	0.56	1.48	0.19	0.45
	MP2	0.88	1.94	0.30	1.00

[a] Experimental values for k_e(Au-Au) in Au_2 from ref 29.

Chart I



The geometries of Au_2, $AuPH_3$, and compound **1** have been optimized at both the HF and MP2 levels[27] using energy-adjusted relativistic pseudopotentials for the gold atom. For gold we used rather extensive basis sets, i.e. a (9s/6p/5d)/[8s/3p/4d] basis set at the nonrelativistic (NR) level and a (8s/6p/5d)/[7s/3p/4d] basis set at the relativistic (R) level. The basis set exponents and multielectron adjusted pseudopotential parameters for gold are described elsewhere.[19] For the hydrogen and phosphorus atoms, we used 21G and 4-31G* basis sets, respectively.[27,28] The results are listed in Tables I–III.

The optimized structure of **1** is the linear P–Au–Au–P unit. P–Au–Au–P trans bending results in a pure repulsive curve, Figure 1. The calculated Au–P bond distance of 2.44 Å is much larger compared to common bond lengths published for Au^I compounds (2.22–2.33 Å).[31] However, compound **1** is a Au^0 species, and we expect slightly larger Au–P bond distances compared to Au^I compounds (in the reported structure[5] of bent $Au_2(PPh_3)_2$, the Au–P distance is 2.37 Å). An increase is basis set quality on both the gold and phosphorus atoms may shorten the Au–P bond length.[32] Note that at the measured P–Au–Au bond angle of $Au_2(PPh_3)_2$ published by Mingos (α = 129°)[5] repulsive forces are very large, i.e. ca 116 kJ/mol at the relativistic MP2 level (neglecting relaxation effects). This is 58 kJ/mol for each Au–P unit; hence, the proposed agostic interaction between the phenyl ortho hydrogen and the Au_2 center in $Au_2(PPh_3)_2$ must be unusually high and this may be due to relativistic effects.[33] Moreover, the RMP2 Au–Au bond distance in **1** is considerably shorter compared to the value given by Mingos[5] (2.76 Å), which indicates strong agostic H interactions.

The relativistic MP2 (RMP2) gold bond distance, dissociation energy (Table I), and force constant (Table II) for Au_2 are in reasonable agreement with experimental data. To achieve higher accuracy, more diffuse functions as well as f functions have to be added; i.e., a gold (8s/6p/5d/1f)/[7s/3p/4d/1f] basis set results in a RMP2 dissociation energy of 218 kJ/mol and a bond distance of 2.50 Å for Au_2,[34] which is in excellent agreement with the experimental data (221 kJ/mol and 2.47 Å).[29] This shows that the MP2 method is a quite accurate correlation method for the gold–gold interaction.[32] Relativistic effects increase significantly correlation contributions in $D_e(Au_2)$; i.e., compare the HF value ($\Delta_R D_e(Au_2)$ = −32.7 kJ/mol) with the MP2 result ($\Delta_R D_e(Au_2)$ = −76.8 kJ/mol). This can be understood from the relativistic 6s contraction, which leads to an increased electron density within the valence region and therefore leads to an increase in electron correlation. Similar effects are calculated for the dinuclear compound **1** (Table I); i.e., electron correlation changes $\Delta_R D_e(PH_3Au–AuPH_3)$ by 54 kJ/mol. The phosphine ligands increase the dissociation energies at both levels of theory (NR and R) compared to Au_2 and this results in a very large relativistic change of D_e at the MP2 level, $\Delta_R D_e(Au_2(PH_3)_2)$ = −138.8 kJ/mol. We expect that even larger relativistic changes are

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Table III. HF and MP2 Mulliken Atomic Orbital Populations n and Gross Atomic Charges q for Au and P

		Au				P			
molecule	method	n(s)	n(p)	n(d)	q	n(s)	n(p)	n(d)	q
PH_3	NRHF					1.79	3.28	0.15	−0.21
	NRMP2					1.80	3.31	0.16	−0.26
Au_2	NRHF	0.94	0.06	10.0	0				
	NRMP2	0.94	0.07	9.99	0				
	RHF	1.04	0.02	9.94	0				
	RMP2	1.11	0.01	9.88	0				
$AuPH_3$	NRHF	1.01	0.03	10.01	−0.05	1.77	3.27	0.15	−0.19
	NRMP2	1.01	0.14	9.98	−0.13	1.75	3.32	0.16	−0.23
	RHF	1.01	0.04	10.02	−0.08	1.77	3.24	0.15	−0.16
	RMP2	1.17	0.20	9.81	−0.18	1.72	3.33	0.19	−0.25
$Au_2(PH_3)_2$	NRHF	0.84	0.33	9.92	−0.09	1.76	3.31	0.15	−0.22
	NRMP2	0.76	0.49	9.82	−0.07	1.78	3.37	0.16	−0.31
	RHF	1.22	0.17	9.73	−0.12	1.71	3.33	0.16	−0.22
	RMP2	1.41	0.17	9.59	−0.17	1.69	3.36	0.19	−0.24

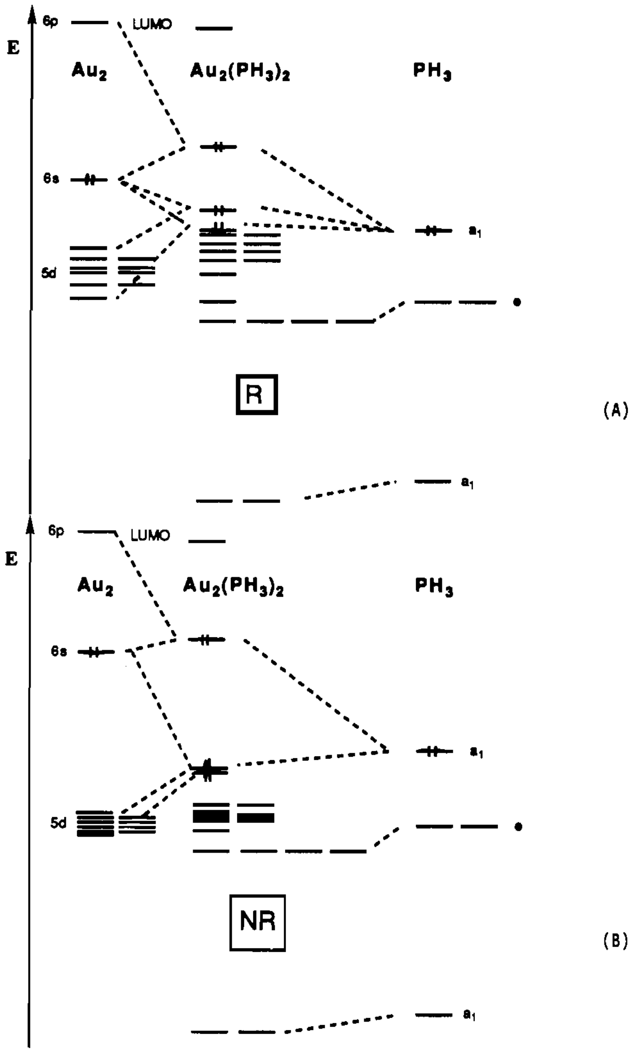

Figure 2. Qualitative MO scheme for the bonding in $Au_2(PH_3)_2$ for the relativistic (A) and nonrelativistic (B) cases.

achieved by improving the basis sets, as this is the case for diatomic Au_2.[34] Table II shows that Au–Au stretching force constants also increase as a consequence of both relativistic effects and the influence of the phosphine ligands. To summarize, (i) relativistic effects stablize the Au–Au bond in $Au_2(PPh_3)_2$ as is the case for diatomic Au_2,[19] and (ii) phosphine ligands play a very important role in stabilizing gold cluster compounds, as suggested by Mingos for the species $Au_6(PR_3)_6^{2+}$ and $Au_9(PR_3)_8^{3+}$.[7]

To analyze the role of the phosphine ligands in gold–gold bonding in more detail, we performed HF and MP2 Mulliken population analyses for the different gold compounds (Table III). As pointed out before,[19] Au(5d) and Au(6p) participation is very small in Au_2 and can be neglected (Table III). However, for the $Au_2(PH_3)_2$ compound, Au(5d) and Au(6p) participations are substantial. Obviously, phosphine ligands activate Au(5d) and Au(6p) orbitals and stabilize the Au–Au bond.[35] The population analysis for the mononuclear compound $AuPH_3$ shows that the PH_3 ligand donates electron density toward the gold radical (negative charge q at the gold atom, Table III), which results in an increased stability in the Au–Au bond when undergoing dimerization.

The MO scheme for the bonding in $Au_2(PH_3)_2$ is shown in Figure 2. Note the relativistic increase in the Au(5d)/Au(6s) gap in both compounds, Au_2 and $Au_2(PH_3)_2$. It is sufficient to discuss only the first three HOMOs (in the sequence of orbital energies $2a_1'$, a_2'', and $1a_1'$), which are shown schematically in Chart I and in Figure 2. Figure 2 and an analysis of the orbital coefficients show that the $2a_1'$ orbital consists of large Au(6p) admixture and the two lower lying a_2'' and $1a_1'$ orbitals have large Au(5d) contributions. These contributions are significantly increased by relativistic effects.

We expect similar results for gold cluster compounds of higher nuclearity. Finally, we point out that the $AuPH_3$ radical is not very stable at the MP2 level with respect to dissociation into Au and PH_3, despite the fact that this moiety is often used for isolobal analogies to the hydrogen atom.[3,23,36] In contrast, the positively charged species $AuPH_3^+$ is stable.[23]

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(35) This was suggested before by Mingos using a semiempirical Extended Hückel approach.[7a]

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Difluorodinitrosomethane, $ONCF_2NO$, and Hexafluorodinitrosopropane, $ONCF_2CF_2CF_2NO$

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Since trifluoronitrosomethane, CF_3NO, was first reported by Ruff and Giese in 1936, this stable blue compound and its derivatives have been studied extensively.[1] Its synthesis from the