# Theory of the $d^{10}$–$d^{10}$ Closed-Shell Attraction: 1. Dimers Near Equilibrium**

**Pekka Pyykkö,* Nino Runeberg and Fernando Mendizabal**

**Abstract**: We study the dependence of the aurophilic attraction ($Au^I$–$Au^I$) in perpendicular model systems of the type $[(ClAuPH_3)_2]$ on the ab initio method, basis set and different pseudopotentials used, and on relativity. The effects of varying the "halogen" (X = F, H, Cl, Me, Br, -C≡CH, I), the "phosphine" (L = $PH_3$, $PMe_3$, -N≡CH) and the metal (M = Cu, Ag, Au) on the M–M′ interaction of the $[(XML)_2]$ dimer are also studied. The depth of the interaction potential increases with the softness of the group X. It decreases by 27% for M = Au, X = Cl and L = $PH_3$ if relativistic effects are omitted at fixed geometry.

**Keywords**
ab initio calculations · bond theory · closed-shell attraction · gold · relativistic effects

## Introduction

From crystallography, NMR spectroscopy,[1, 2] Raman spectroscopy[3] and theory[4–6] there is evidence for weak attractions between $d^{10}$ cations. In the case of gold(I), Schmidbaur[2] uses the term aurophilic attraction for intra- and intermolecular $Au^I$–$Au^I$ contacts. In general, these interactions may be referred to as metallophilic attractions[5] and are found in both inorganic and organometallic compounds. They are weaker than most covalent or ionic bonds, but stronger than other van der Waals bonds and comparable in strength to typical hydrogen bonds.

In the case of small mononuclear gold complexes, the van der Waals gold–gold contacts are typically 305–350 pm, associated with a bond energy of the order of 21–46 $kJ\,mol^{-1}$.[7–9] In particular, gold(I) complexes of type L-Au-X (L = donor ligands, X = halide or pseudohalide) can be aggregated into dimers, oligomers or polymers. The degree of oligomerization is determined by a number of factors, among which the steric effect of the ligands is the most clear.[10] This aggregation might also be described as a supramolecular chemistry of gold compounds.[11] Also, other oxidized or neutral closed-shell metal atoms, for instance, $Cu^I$, $Hg^0$ or $Tl^I$, can undergo intermolecular aggregation through short van der Waals metal–metal contacts.[6, 11–15]

We have presented theoretical evidence that these attractions are pure correlation effects, strengthened by relativistic effects.[5, 6, 13, 16, 17] The absence of any attraction at Hartree–Fock (HF) level does not support the idea of predominant hybridization effects between the filled $(n-1)$d orbitals and the $n$s and $n$p orbitals,[18, 19] or an analogous explanation to that used for $ns^2$ ions, such as $Tl^I$.[20] In all the cases where there are inter- or intramolecular metal–metal attractions, the correlation effects are essential; at the HF level, repulsive interactions are obtained instead. Hence, it is necessary to use at least MP2-level methods for the description of the dispersion forces, which are included among the correlation effects.[4, 21] Our earlier work was typically carried out at MP2 level, using 11 or 19 valence electron (VE) pseudopotentials and sometimes adding polarization functions.

Here, we first examine technicalities, like the influence of the basis sets, ab initio methods and pseudopotentials used, and the explicit influence of relativity, which was not previously studied for the free dimers. We then return to the influence of the various ligands (X and L) on the interaction potential, $V(R_e)$, for the $[(XML)_2]$ dimer models. Typically X is Cl and L $PH_3$. Here $R_e$ stands for the optimized M–M distance. We also consider the mixed-metal dimers (M, M′ = Cu, Ag, Au).

The present studies were carried out on the perpendicular $[(XML)_2]$ dimers of $C_2$ symmetry shown in Figure 1. At this geometry the electrostatic dipole–dipole interaction vanishes. We emphasize that we are not looking for the absolute minimum

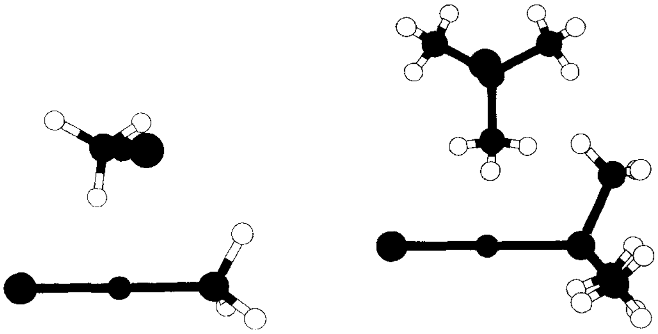

Figure 1. The assumed structures of the dimeric models. Left: $[(XMPH_3)_2]$. Right: $[(ClAuPMe_3)_2]$.

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[**] Theory of the $d^{10}$–$d^{10}$ Closed-Shell Attraction, Part 1. Part 2: following paper.

0947-6539/97/0309-1451 $ 17.50+.50/0

of the gas-phase dimer, but rather studying the necessary technical requirements for a credible treatment of the aurophilic attraction, at a typical crystallographic geometry.

## Computational Details

The Gaussian 94 package[22] was used. The basis sets and pseudopotentials (PPs) used in the production runs are given in Table 1. The 19-VE quasi-relativistic (QR) pseudopotentials of Andrae,[23] Schwerdtfeger (QR and non-relativistic, NR),[24] and Stevens,[25] and 11-VE "LANL1DZ"[26] were employed for gold. The silver[23] and copper[27] atoms were treated by a 19-VE Stuttgart PP. Moreover, the atoms C, P and halogens were treated by 4-VE, 5-VE and 7-VE PPs, respectively, of ref. [28].

Table 1. Basis sets and pseudopotentials (PPs) used in the present work. The same nonmetal basis was used in every case. The metal calculations are labelled as cases 1–14.

| Case | Atom | PP | Basis | Remarks |
|---|---|---|---|---|
| | H | – | (4s 1p)/[2s 1p] | $\alpha_p = 0.8$ [30] |
| | C | Bergner [28] | (4s 4p 1d)/[2s 2p 1d] | $\alpha_p = 0.1561$, $\alpha_d = 0.80$ |
| | P | Bergner [28] | (4s 4p 1d)/[2s 2p 1d] | $\alpha_p = 0.084$, $\alpha_d = 0.34$ |
| | F | Bergner [28] | (4s 4p 1d)/[2s 2p 1d] | $\alpha_p = 0.0848$, $\alpha_d = 1.496$ |
| | Cl | Bergner [28] | (4s 4p 1d)/[2s 2p 1d] | $\alpha_p = 0.0154$, $\alpha_d = 0.514$ |
| | Br | Bergner [28] | (4s 4p 1d)/[2s 2p 1d] | $\alpha_p = 0.0361$, $\alpha_d = 0.389$ |
| | I | Bergner [28] | (4s 4p 1d)/[2s 2p 1d] | $\alpha_p = 0.0326$, $\alpha_d = 0.266$ |
| 1 | Au | Andrae [23] | (8s 6p 5d 1f)/[6s 5p 3d 1f] | $\alpha_f = 0.2$ |
| 2 | Au | Andrae [23] | basis 1 [a] | dito, $\alpha_f = 1.19$ |
| 3 | Au | Andrae [23] | (8s 6p 5d 2f)/[6s 5p 3d 2f] | $\alpha_f = 0.2, 1.19$ |
| 4 | Au | Andrae [23] | (9s 7p 6d 2f)/[7s 6p 4d 2f] | diffuse s, p, d on Au [b] |
| 5 | Au | Schwerdtfeger R [24] | basis 1 [a] | $\alpha_f = 0.20$ |
| 6 | Au | Stevens [25] | basis 1 [a] | $\alpha_f = 0.20$ |
| 7 | Au | 11-VE LANL1DZ [26] | LANL1DZ basis for Au | $\alpha_f = 0.20$ |
| 8 | Au | Schwerdtfeger NR [24] | basis 1 [a] | $\alpha_f = 0.20$ |
| 9 | Au | 11-VE LANL1DZ [26] | LANL1DZ basis for Au | diffuse s,p on P and Cl [c] |
| 10 | Au | Schwerdtfeger NR [24] | (8s 6p 5d 1f)/[8s 3p 4d 1f] NR | $\alpha_f = 0.20$ |
| 11 | Au | Andrae [23] | (8s 6p 5d 1f)/[7s 5p 3d 1f] | basis R [24], $\alpha_f = 0.2$ |
| 12 | Au | Schwerdtfeger R [24] | (8s 6p 5d 1f)/[7s 3p 4d 1f] R | $\alpha_f = 0.20$ |
| 13 | Ag | Andrae [23] | (8s 6p 5d 2f)/[6s 5p 3d 2f] | $\alpha_f = 0.22, 1.72$ |
| 14 | Cu | Dolg [27] | (8s 6p 5d 2f)/[6s 5p 3d 2f] | $\alpha_f = 0.24, 3.70$ |

[a] The basis 1 is defined as (8s 6p 5d 1f)/[6s 5p 3d 1f]. [b] $\alpha = 0.004377, 0.007974, 0.0189675$ for s, p, d [23], respectively. [c] $\alpha = 0.035, 0.040$ for s,p on P and $\alpha = 0.059$ for s on Cl.

We employed one or two f-type polarization functions for Au, Ag and Cu. The diffuse f orbital is necessary for the intermolecular interaction and the compact f orbital as polarization fuction in intramolecular bonding. The diffuse f orbital exponent was obtained by maximizing the $M^I$ cation MP2 electric dipole polarizability and the compact f by minimizing the CCSD(T) total energy of the $M^0$ atom (see Table 1).

For the C, P and halogen atoms the double-zeta basis sets of ref. [28] were used, augmented by d-type polarization functions.[29] For the H atom, double-zeta plus one p-type polarization function was used.[30]

We first fully optimized the geometries for the $[XMPH_3]$ and $[ClAuPMe_3]$ monomers at the MP2 level (see Tables 2–4). We used these geometries for studying the $M^I$–$M^I$ intermolecular interactions. The interaction energy $V(R)$ of the dimers was obtained according to Equation (1); a counterpoise correction for the basis-set superposition error (BSSE)[31] on $\Delta E$ was thereby performed. The calculations were mostly carried out at MP2 level. Furthermore, we studied the effect of the correlation at higher MP*n* and CCSD(T) levels in the dimers $[(ClAuPH_3)_2]$ and $[(HAuPH_3)_2]$, respectively.

$$\Delta E = E_{AB}^{(AB)} - E_{A}^{(AB)} - E_{B}^{(AB)} = V(R) \quad (1)$$

Table 2. Optimized geometries for the $ClMPH_3$ monomers at MP2 level. The HF values are given in parentheses. Distances in pm; HPM angle in degrees; energy in au.

| M | Basis | P–H | P–M | M–Cl | HPM | *E* |
|---|---|---|---|---|---|---|
| Au | 1 | 141.4 | 226.6 | 227.9 | 117.6 | −158.20488 |
| | | (140.8 | 234.6 | 234.1 | 117.3) | |
| Au | 2 | 141.3 | 222.4 | 226.2 | 117.8 | −158.42017 |
| Au | 3 | 141.3 | 224.3 | 226.3 | 117.4 | −158.47013 [a] |
| Au | 4 | 141.3 | 224.3 | 226.3 | 117.4 | −158.47159 |
| Au | 5 | 141.4 | 226.6 | 227.9 | 117.6 | −158.38253 |
| Au | 6 | 141.6 | 227.5 | 228.7 | 117.6 | −158.21902 |
| Au | 7 | 141.2 | 237.7 | 239.1 | 117.6 | −56.704699 |
| Au | 8 | 141.5 | 254.6 | 243.8 | 119.0 | −153.90693 |
| Au | 9 | 141.2 | 235.9 | 238.3 | 117.7 | −56.712167 |
| Au | 12 | 141.3 | 227.5 | 229.1 | 117.7 | −158.35343 |
| Ag | 13 | 141.5 | 232.5 | 227.4 | 118.4 | −169.72845 |
| Cu | 14 | 141.5 | 211.9 | 206.5 | 118.5 | −220.02072 |

[a] Later taken as standard monomer geometry.

Table 3. Optimized geometries and experimental results for the $[ClAuPMe_3]$ monomers at MP2 level. Distances in pm; energy in au.

| System | Basis | P–C | P–Au | Au–Cl | C–H | CPAu | HCP | *E* |
|---|---|---|---|---|---|---|---|---|
| Au | 15 | 185.9 | 224.3 | 227.5 | 109.7 | 113.9 | 109.8 | −178.949688 |
| Exp. | [a] | 180.0 | 223.3 | 230.9 | – | – | | |

[a] Ref. [36], chloro(trimethylphosphine)gold(I); chain structure.

Table 4. Optimized geometries for the $[XAuPH_3]$ [a] monomers at MP2 level. Distances in pm; energy in au.

| X | P–H | P–Au | Au–X | HPAu | *E* |
|---|---|---|---|---|---|
| F | 141.3 | 221.3 | 196.3 | 117.3 | −167.70254 |
| H | 141.6 | 234.5 | 157.3 | 118.5 | −144.11072 |
| Cl | 141.3 | 224.3 | 226.3 | 117.4 | −158.47013 |
| $CH_3$ | 141.7 | 233.1 | 203.6 | 118.7 | −150.93618 |
| Br | 141.4 | 225.6 | 238.8 | 117.5 | −156.84562 |
| HCC | 141.5 | 230.0 | 195.2 | 118.0 | −155.32439 |
| I | 141.4 | 226.9 | 255.9 | 117.6 | −154.87424 |

[a] Basis 3 for gold.

**Editorial Board Member:**[*] *Pekka Pyykkö was born 1941 in Hinnerjoki, Finland, and received his formal education in the nearby city of Turku culminating with a Ph.D. in 1967. After working at the Universities of Aarhus, Göteborg, Helsinki, Jyväkylä, Paris and Oulu between 1968 and 1974, he became Associate Professor of Quantum Chemistry at Åbo Akademi in Turku (1974–1984). He has held the Swedish Chair of Chemistry at the University of Helsinki since 1984, and is a Research Professor of The Academy of Finland (1995–2000). He is also the Chairman of the REHE Programme of the ESF. He started off as an NMR spectroscopist and published his first paper on relativistic effects in 1971. In addition to various aspects of heavy-element chemistry, his current interests include the search for and understanding of new chemical species, and the determination of nuclear quadrupole moments from high-precision quantum chemistry and spectroscopic data.*

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Table 5. Optimized M–M distances, $R_e$, for the [(ClMPH$_3$)$_2$] and [(ClAuPMe$_3$)$_2$] dimers at various levels of theory. Distance $R_e$ in pm; interaction energy $V(R_e)$ in au; force constant $F$(MM') in $10^2$ N m$^{-1}$ (= 1 mdyn Å$^{-1}$).

| M | Case | $R_e$ | $V(R_e)$ | $F$ |
|---|---|---|---|---|
| Au | 1 [a] | 330.3 | −0.007494 | 0.111784 |
| Au | 2 [a] | 341.1 | −0.005594 | 0.075126 |
| Au | 3 [a] | 320.8 | −0.009407 | 0.140959 |
| Au | 4 [a] | 320.8 | −0.009485 | 0.140572 |
| Au | 5 [a] | 330.8 | −0.007411 | 0.109288 |
| Au | 6 [a] | 328.7 | −0.007848 | 0.115687 |
| Au | 7 [a] | 311.1 | −0.011179 | 0.251579 |
| Au | 8 [a] | 332.9 | −0.006301 | 0.104369 |
| Au | 8 [b] | 350.6 | −0.005377 | 0.072533 |
| Au | 9 [a] | 311.2 | −0.011544 | 0.246762 |
| Au | 10 [b] | 352.0 | −0.005319 | 0.071140 |
| Au | 11 [b] | 337.9 | −0.006745 | 0.094451 |
| Au | 12 [a] | 334.8 | −0.007073 | 0.099604 |
| Ag | 13 [a] | 311.3 | −0.008103 | 0.122556 |
| Cu | 14 [a] | 313.7 | −0.004885 | 0.055603 |
| Au | 15 [c] | 375.5 | −0.008451 | 0.043637 |
| Au/Ag | 16 [a] | 314.3 | −0.009066 | 0.148629 |
| Au/Cu | 17 [a] | 314.1 | −0.006944 | 0.094910 |
| Ag/Cu | 18 [a] | 309.7 | −0.006580 | 0.091488 |

[a] Using the optimized monomer geometry. [b] Using the monomer geometry of case 3. [c] Dimer [(ClAuPMe$_3$)$_2$].

Table 6. Optimized Au–Au distances, $R_e$, for [(XAuPH$_3$)$_2$] [a]. Distance $R_e$ in pm; interaction energy $V(R_e)$ in au; force constant $F$(MM') in $10^2$ N m$^{-1}$.

| X | $R_e$ | $V(R_e)$ | $F$ |
|---|---|---|---|
| F | 321.8 | −0.008264 | 0.136309 |
| H | 309.1 | −0.009211 | 0.180949 |
| Cl | 320.8 | −0.009407 | 0.140960 |
| CH$_3$ | 314.2 | −0.009803 | 0.172909 |
| Br | 317.6 | −0.010698 | 0.164329 |
| HCC | 309.9 | −0.011433 | 0.207158 |
| I | 315.4 | −0.012315 | 0.179344 |

[a] Using the optimized monomer geometry.

The optimized interaction energies [$V(R_e)$] and M–M distances ($R_e$) for the dimers are shown in Tables 5 and 6. We fitted the calculated points using the four-parameter Equation (2), which had previously been used[6] to derive

$$V(R) = Ae^{-BR} - CR^{-n} \qquad (2)$$

the Herschbach–Laurie relation.[34] Differentiating Equation (2), we obtain the force constant $F$ [Eq. (3)]. This expression will allow us to compare

$$F(\mathrm{MM'}) = V''(R) = AB^2e^{-BR} - Cn(n+1)R^{-(n+2)} \qquad (3)$$

the available experimental $F$(MM) force constants from Raman spectroscopy[3] with those calculated for free dimers (Tables 5 and 6). In ref. [3] the Herschbach–Laurie equation was used to correlate $F$(Au–Au) with the Au–Au distance over the entire range from Au$_2$ to weak aurophilic interactions. In ref. [6] (see Chapt. II. D. and Figure 36), the bond energy was approximately related to the distance.

## Results and Discussion

**Monomers**: The geometries of the [XMPR$_3$] monomers were fully optimized at MP2 level. A $C_{3v}$ point symmetry was assumed. The optimized geometries are given in the Tables 2–4. For some dimers of gold, experimental crystallographic results are given in Table 7.

The calculated P–Au and X–Au bond lengths were close to experimental values when we used the 19-VE PPs for gold. It did not make any difference whether we used basis sets with 1 or 2f orbitals. This tendency was maintained for [ClAuPR$_3$] and [XAuPH$_3$]. As stated above, the P and X polarization functions are also important (see Tables 2–4).[17] However, the 11-VE LANL1DZ QR PP (case 7) overestimates the bond lengths. The HF or NR bond lengths are also larger than the experimental ones. This emphasizes the importance of 19-VE PPs for gold at MP2 level in the monomers.

**Dimers**: In the Tables 5 and 6, we summarize the interaction energies and equilibrium Au–Au distances. Some representative experimental Au–Au distances are given for comparison in Table 7. The calculated distances fall in the same range as the experimental ones.

Table 7. Selected experimental structural parameters [a] of perpendicular [(XAuPR$_3$)$_2$]. Distances in pm.

| Compound | P–Au | X–Au | Au$^I$–Au$^I$ | Ref. |
|---|---|---|---|---|
| [(ClAuPH$_2$(C$_6$$t$Bu$_3$H$_2$))$_2$] | 224.2 | 228.9 | 344.0 | [35] |
| [(ClAuPMe$_3$)$_2$] | 223.3 | 231.0 | 333.8 [b] | [36] |
| [(ClAuPEt$_3$)$_2$] | 223.9 | 228.4 | 361.5 | [37] |
| [(ClAuPMe$_2$Ph)$_2$] | 223.6 | 231.6 | 323.0 | [39] |
| [(BrAuPMe$_2$Ph)$_2$] | 224.6 | 242.3 | 311.9 | [39] |
| [(IAuPMe$_2$Ph)$_2$] | 225.9 | 258.8 | 310.4 | [39] |
| [(PhCCAuPPh$_3$)$_2$] | 227.1 [b] | 199.7 [b] | 315.4 | [40] |

[a] From X-ray crystal structure determinations. [b] Mean value.

*Effect of pseudopotential on Au*: The basis set was now kept constant for the PPs of Andrae,[23] Schwerdtfeger[24] and Stevens,[25] while for the case of 11-VE LANL1DZ PP we used the basis set of Hay and Wadt[26] (see Table 1). One f orbital with $\alpha_f = 0.20$ was used in all four cases. The interaction energies at MP2 level for the dimers [(ClAuPH$_3$)$_2$] are shown in Figure 2. All three 19-VE PPs are seen to give very similar curves. The 11-VE LANL1DZ PP exaggerates the aurophilic attraction. The HF curves are invariably repulsive.

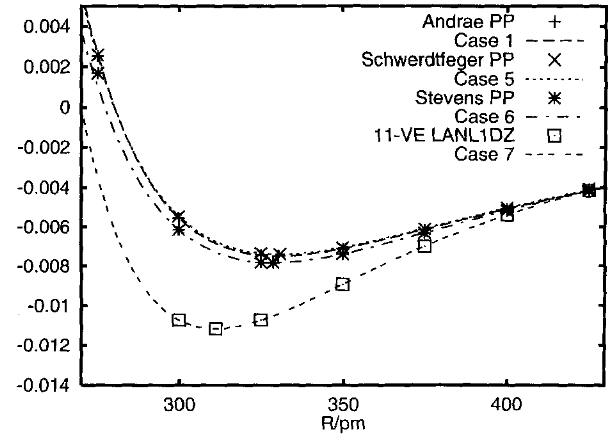

Figure 2. Calculated [(ClAuPH$_3$)$_2$] interaction energies $V(R)$ as function of the pseudopotential used. Calculated points fitted to Eq. (2). The basis sets are defined in Table 1.

As the Andrae and Schwerdtfeger pseudopotentials are energy-adjusted, while the Stevens one is shape-consistent, the very similar results for these three 19-VE pseudopotentials suggest that this difference does not matter. Whether the 11-VE/19-VE difference ultimately arises from the nodal structure (for the correlating 6p orbitals), as suggested by Hay,[32] or from the large Hilbert space in the semicore region, leading to spurious low-lying states, as suggested for indium by Leininger et al.,[33] cannot be answered here.

*Effect of the basis set*: We show the effect of the basis set for the pseudopotential of Andrae in Figure 3. It can be seen that adding $\alpha_f = 1.19$ to the previously used $\alpha_f = 0.2$ improves the interaction energy. The use of 1.19 instead of 0.2 is not advisable. Further addition of diffuse s, p and d functions on Au to the 2f case gives minimal improvement. In this direction the basis appears to be saturated.

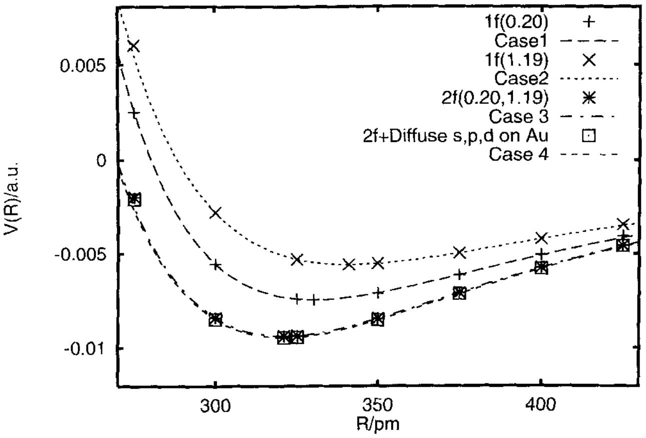

Figure 3. The effect of changing or augmenting the Au basis set from the previously used 1 f ($\alpha_f = 0.2$) case (Andrae PP, $[(ClAuPH_3)_2]$).

*Relativistic effects*: The importance of relativistic effects for the aurophilic attraction was already suggested by the Ag/Au comparison in our first paper[4] and explicitly demonstrated for the A-frames.[17] It has not been explicitly studied before for the free dimers.

The results in Figure 4 show that, for the same monomer geometry, the interaction energy in $[(ClAuPH_3)_2]$ decreases by 27% (from $-0.007411$ to $-0.005377$ au) on going from relativistic to nonrelativistic pseudopotentials. This is the relativistic effect due to electronic reorganization. If the NR monomer geometry is reoptimized, the $V(R_e)$ becomes $-0.006301$ au, a decrease of only 15%. These are the cases 8a and 8b, respectively. Thus the relativistic effect is there, but it should not be overemphasized.

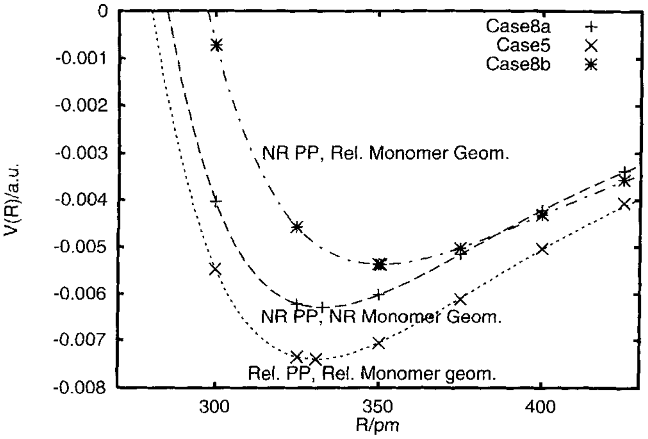

Figure 4. The effect of relativity on the aurophilic attraction in the perpendicular $[(ClAuPH_3)_2]$ dimer (Schwerdtfeger PP, $\alpha_f = 0.20$).

**Effect of the Ligand X in $[(XAuPH_3)_2]$**: The effect of the ligand X in this dimer series has been studied before.[5] It was concluded that the softer X is, the stronger is the interaction. We have now repeated the same study at the improved 2f-function level, and have additionally examined the case X = -C≡CH. The results, at MP2 level, are shown in Figure 5 and Table 6. The interaction depth, $V(R_e)$, increases with the softness of the ligand in the order shown in series (4).

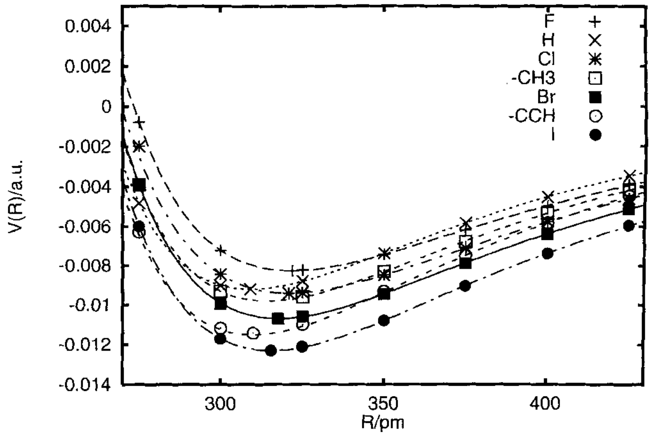

Figure 5. The effect of the group X on the Au–Au interaction in $[(XAuPH_3)_2]$.

$$F < H < Cl < Me < Br < HCC\text{-} < I \qquad (4)$$

When these results are compared with the previous study,[5] it is observed that the tendency in the series is maintained. However, when one f orbital on Au is employed for the halide ligands, the interaction energies and Au–Au distances are on average 34% smaller and 5% larger, respectively, than the values obtained when using two f orbitals. Also, the force constant $F$(AuAu) is now enhanced by 36.5%. The corresponding experimental results based on Raman studies are described in references [3,38].

For the halide ligands the calculated $V(R_e)$ show a correlation with $R_e$; the same is possibly true for the hydrocarbon ligands as well (see Figure 6). The experimental data on the series of binuclear complexes $[(XAuPMe_2Ph)_2]$ (X = Cl, Br, I)[39] given in Table 7 allow us to compare our results on the model $[(XAuPH_3)_2]$ (Table 6) with the observed effect of the halide ligand on the Au–Au interaction. In both cases, the Au–Au distance decreases in the order Cl > Br > I. The calculated Au–Au distance of 309.9 pm for the dimer $[(HCCAuPH_3)_2]$ is not far from the experimental value of 315.4 pm for compound $[(PhCCAuPPh_3)_2]$[40] (see Table 7).

We tried to correlate $V(R_e)$ with various parameters (e.g., Au Mulliken charge, NBO charge, dipolar moments, HOMO and LUMO energies), only with success for the halides. A plot against the calculated monomer MP2 Au NBO charge is shown in Figure 7.

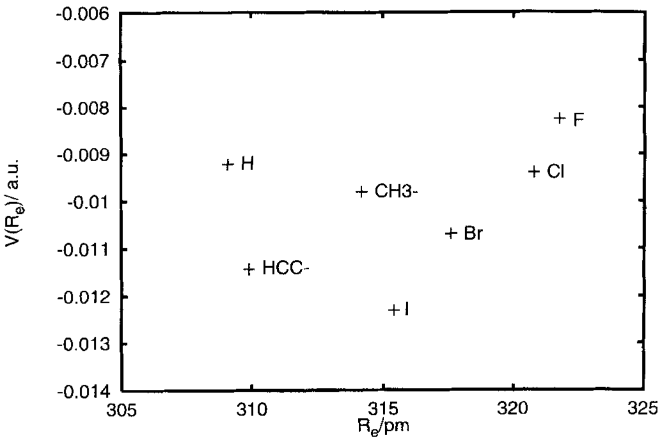

Figure 6. The dependence of the $V(R_e)$ on $R_e$ for the $[(XAuPH_3)_2]$ dimers.

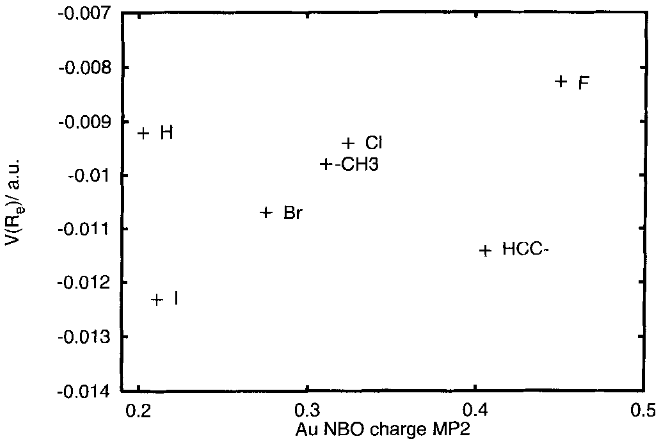

Figure 7. The dependence of the $V(R_e)$ on the NBO charge of the gold atom for the $[(XAuPH_3)_2]$ dimers.

**Effect of the "Phosphine" (L = $-PR_3$ and $-N{\equiv}CH$)**: We now consider the $V(R)$ for dimer $[(XAuL)_2]$ as a function of the distance $R$ (Au–Au) for several phosphines $PR_3$ (R = H, Me) and $-N{\equiv}CH$, using the case 3 parameters in Table 1 for all dimers.

The effect of the group L in the dimers, at the MP2 level, is given in the Figure 8. The dimer with trimethylphosphine gives a very flat minimum. The calculated interaction energy for X = $PMe_3$ is 11 % smaller than for X = $PH_3$, and the equilibrium distance increases from 320.8 pm for X = $PH_3$ to 375.7 pm for X = $PMe_3$ (Table 8). We may possibly be seeing a balance between two competing effects, namely, the larger size of $PMe_3$ weakening interaction and its softer nature strengthening interaction.

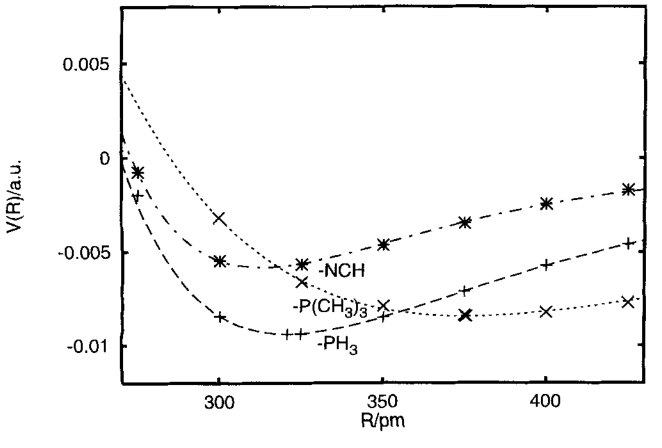

Figure 8. The effect of the "phosphine" L (L = $PH_3$, $PMe_3$ or $-N{\equiv}CH$) on the $[(XAuL)_2]$ interaction.

Table 8. Effect of the group L in $[(XAuL)_2]$. Distances in pm; energy in au.

| Compound | Case | $R_e$ | $V(R_e)$ |
|---|---|---|---|
| $[(HAuNCH)_2]$ | 19 | 312.8 | −0.005826 |
| $[(ClAuPH_3)_2]$ | 3 | 320.8 | −0.009407 |
| $[(ClAuPMe_3)_2]$ | 15 | 375.5 | −0.008451 |
| $[ClAuPMe_3]$ | exp. [a] | 333.8 [c] | – |
| $[ClAuPEt_3]$ | exp. [b] | 361.5 | – |

[a] Ref. [36], chloro(trimethylphosphine)gold(I). [b] Ref. [37], chloro(triethylphosphine)gold(I). [c] Mean value.

Experimentally, chloro(trimethylphosphine)gold(I) is found to have one asymmetric unit cell, containing three crystallographically independent molecules.[36] These units show an aggregation through Au–Au interactions to form a polymeric chain structure, with distances between gold atoms of 333 pm, on average. This typical aurophilic distance is much shorter than our calculated result in the dimer. The comparison of the crystal data with dimer calculations is obviously complicated by the steric and cooperative effects in the crystal. In the chloro(triethylphosphine)gold(I) dimers, Au–Au contacts are actually formed with a large intermetallic distance of 361.5 pm (Table 8).[37]

**Higher-Level Methods in $[(XAuPH_3)_2]$**: We now consider the effect of the electronic correlation in the dimers $[(XAuPH_3)_2]$ with X = Cl and H at MP4(SDQ) and CCSD(T) level, respectively. The Au–Au distances in both dimers are kept equal to those calculated at MP2 level. The basis set and PP correspond to case 3.

The interaction energies for both dimers are shown in Table 9 at HF, MP2, MP3, MP4(SDQ) and CCSD(T) levels. Figure 9 shows the effect of these various methods on the interaction energy (energy at MP2 level normalized as +1) for the systems $[(XAuPH_3)_2]$ (X = H and Cl). The trend for the individual contributions[41, 42] in Table 10 is similar for the two systems. The central conclusion here is that the MP2-level interaction energy, $\Delta E$(MP2), nearly vanishes at the MP3 level for both systems. At MP4 level 60 and 54% of the MP2 result are recovered for

Table 9. Effect of method on the interaction energy of systems $[(XAuPH_3)_2]$. Energy in au.

| Method | $[(ClAuPH_3)_2]$ [a] | $[(HAuPH_3)_2]$ [b] |
|---|---|---|
| $\Delta E$(HF) | 0.006062 | 0.007506 |
| $\Delta E$(MP2) | −0.009415 | −0.009195 |
| $\Delta E$(MP3) | −0.000611 | 0.000526 |
| $\Delta E$(MP4(SDQ)) | −0.005659 | −0.004947 |
| $\Delta E$(CCSD) | – | −0.002279 |
| $\Delta E$(CCSD(T)) | – | −0.004384 |

[a] Au–Au distance is 320.8 pm. [b] Au–Au distance is 309.1 pm.

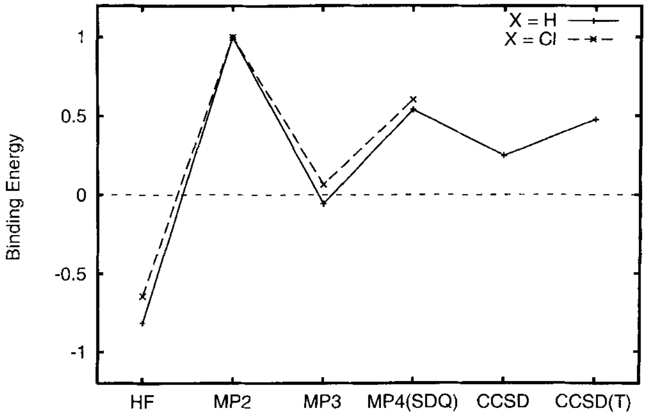

Figure 9. Effect of the method used on the interaction energy (value at MP2 level normalized to +1) of systems $[(XMPH_3)_2]$ at the MP2 minimum-energy geometry.

Table 10. The separated second-, third- and fourth-order contributions to the interaction energy in $[(XAuPH_3)_2]$. Energy in au.

| Method | $[(ClAuPH_3)_2]$ | $[(HAuPH_3)_2]$ |
|---|---|---|
| $\Delta E^{HF}$ | 0.006062 | 0.007506 |
| $\Delta E^2_D$ | −0.015478 | −0.016701 |
| $\Delta E^3_D$ | 0.008804 | 0.009721 |
| $\Delta E^4_{SDQ}$ | −0.005048 | −0.005473 |

the two systems, respectively. The triplets between CCSD and CCSD(T) also contribute strongly. The importance of the triple excitation has already been noted by Hobza and Zahradnik.[42] They are the lowest ones coupling intra- and intermolecular correlation.

Szabo and Ostlund[43] showed that the MP2 supermolecular interaction energy corresponds to the dynamic polarizabilities calculated at the "uncoupled" level, with $\Delta E = \varepsilon_a - \varepsilon_i$ energy denominators. The more accurate "coupled" level has Coulomb and exchange corrections in $\Delta E$.

The present calculations are at the limit of what is currently possible for systems of the present type. Major methodological work is needed to pinpoint the exact answer.

### Effect of The Coinage Metal (M) in $[(ClMPH_3)_2]$:

*The $[(ClMPH_3)_2]$ systems*: We studied the series M = Au, Ag and Cu in the perpendicular ($C_2$) dimers $[(ClMPH_3)_2]$ (Figure 1, left). For the three metals, we used 19-VE PPs and basis sets with two f orbitals.

Figure 10 shows the interaction energy at MP2 level for the homoatomic $M^I-M^I$ van der Waals interactions, calculated with the monomer geometries given in Table 2. The $V(R_e)$ and $R_e$ values are shown in Table 5, and they are labelled as cases 3, 13 and 14, for gold, silver and copper, respectively. The metal–metal distances for the three cases are close (320.8 to 313.7 pm), but the interaction energy for the silver and copper dimers are 13.8 and 48.1% smaller than that for gold. We note that silver is both smaller and more weakly bound than gold. The calculated Cu–Cu distance is much longer than the typical experimental $Cu^I-Cu^I$ distances in the (mostly bridged) systems studied so far.[6] It is hence not evident that the free dimer is a good model for the compact 3d shells.

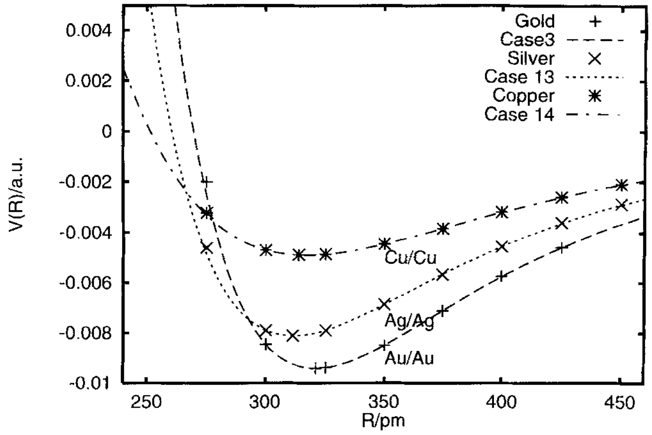

Figure 10. The effect of the metal M on the $[(ClMPH_3)_2]$ interaction.

*The $[(ClMPH_3)(ClM'PH_3)]$ systems*: In the mixed-metal systems (Au/Ag, Au/Cu and Ag/Cu), we again used the optimized monomer geometries for each case. The results are shown in Figure 11 and Table 5 (cases 16–18). The $M^I-(M')^I$ distances span the narrow range between 309.7 and 314.4 pm. The interaction energies increase in the order given in series (5) and lie

$$Ag/Cu < Au/Cu < Au/Ag \quad (5)$$

roughly half-way between the values for the corresponding single-metal systems in each case.

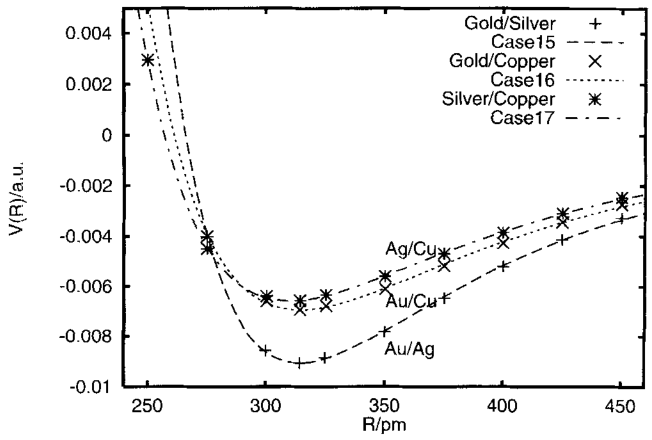

Figure 11. The interaction potentials in heteroatomic systems $[(ClMPH_3)(ClM'PH_3)]$.

## Conclusions

The present free-dimer studies provide further support for the idea[4] that the aurophilic attraction is a correlation effect, strengthened by relativistic contributions. The following points summarize the technical details required to describe this interaction:

1) Increasing the f basis from 1f to 2f strengthens the interaction. Diffuse s, p and d functions on Au are not needed.
2) All three 19-VE pseudopotentials give similar results; 11-VE LANL1DZ exaggerates the attraction and should be avoided, if possible.

3) The interaction energy survives at the higher levels of correlation, on going from MP2 to MP3, MP4(SDQ), CCSD and CCSD(T), but the values obtained in this series oscillate quite strongly. This area will require further study.
4) If relativistic effects are omitted, at constant monomer geometry, the $[(ClAuPH_3)_2]$ attraction $V(R_e)$ decreases by not more than 27%, and even less if the nonrelativistic monomer geometry is reoptimized.
5) $R_e$(Ag–Ag) is slightly shorter and weaker than $R_e$(Au–Au).
6) The mixed-metal interaction potentials $V$(M–M′) lie between the corresponding $V$(M–M) and $V$(M′-M′).
7) In the $[(XAuPH_3)_2]$ series, the softer halogens X yield shorter and stronger Au–Au interactions.

The nature of the interaction and its long-distance limits are discussed in Part 2 of this series.

**Acknowledgment**: P. Pyykkö thanks Hubert Schmidbaur for originally calling his attention to the aurophilic attraction and The Academy of Finland (FA) for a Research Professorship from August 1995 to July 2000. N. R. and F. M. are supported also by FA. DEC Alpha Stations of our laboratory and computer resources from the Center for Scientific Computing (CSC), Espoo, were used in this research.

Received: January 21, 1997 [F 595]

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