Theoretical study of the d^{10}–d^8 interaction between Au(I) and Au(III) on the *cis/trans*-[PH$_3$Au(I)C(L)=C(L)Au(III)(R)$_2$PH$_3$] (R = –H, –CH$_3$; L = –H, –CH$_3$) systems

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Abstract

We have carried out an ab initio study designed to shed some light on the aurophilic attractions between Au(I) and Au(III) in the [PH$_3$Au(I)C(L)=C(L)Au(III)(R)$_2$PH$_3$] (where R = –H, –CH$_3$; L = –H, –CH$_3$) model. Calculations carried out at the MP2 level revealed important facts such as the presence of an intramolecular aurophilic interaction in the *cis*-complexes that stabilizes them with respect to the *trans*-isomers. Using two additional models to study the intermolecular interaction between Au(I) and Au(III) we were able to estimate an interaction energy between 21 and 25 kJ mol^{-1} at the MP2 level of calculation.

1. Introduction

The interaction between two closed shell cations has always been described as a repulsion term. However, this is not the case for certain inorganic and organometallic compounds, where experimental and theoretical evidence exists for attractive interactions between cations with d^8–d^{10}–s^2 configurations at both intra- and intermolecular levels [1–5]. It is worth noting that these interactions are weaker than covalent or ionic bonds, but stronger than other van der Waals bonds. Also, they are comparable in strength to some hydrogen bonds (20–50 kJ mol^{-1}). This phenomenon is known as metallophilic attraction, and particularly for gold, it is designated as aurophilic attraction [6,7].

From a theoretical point of view, metallophilic and in particular aurophilic attractions are interesting because when electronic correlation effects are taken into account, strengthened by relativistic effects, this phenomenon can be quantified [8,9]. Thus, the nature of these interactions can be studied by comparing calculations carried out at both Hartree–Fock (HF) and second-order Møller–Plesset (MP2) levels for a given model system. Hence, it is necessary to perform calculations at

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least at the MP2 level for the proper description of the dispersion forces, with additional allowance for virtual charge-transfer terms, which are included among the correlation effects [10,11].

On the other hand, calculations based on density functional theory (DFT) in aurophilic attractions are not adequate due to the fact that the interaction energy near the van der Waals minimum is unreliable, because the specific form of correlation energy is not properly described [6,12], although certain functionals may be able to mimic the process near equilibrium distance (R_e). Specifically, at the level of the weakest chemical interactions, e.g., van der Waals interactions, DFT apparently fails [13].

Among the many different metals (closed-shell ions) that show this kind of d^8–d^{10} intramolecular attractions and that have been reported so far systems such as Au(I)–Au(III), Au(I)–Pd(II), Au(I)–Ir(I) [14–16] are involved.

In particular, the system of our interest that shows d^8–d^{10} interactions is the [P(CH$_3$)$_3$Au(I) C(CF$_3$)=C(CF$_3$)Au(III)(CH$_3$)$_2$P(CH$_3$)$_3$] complex [17]. The experimental distance between Au(I) and Au(III) centers has been reported to be 331 pm in the *cis*-isomer, pointing to an intramolecular interaction. This suggests that an aurophilic interaction is present in this complex. Also, other clusters with short Au(I)–Au(III) contacts that also show intramolecular interactions have been studied in the past, namely: [Se(AuPPh$_3$)$_2$ {Au(C$_6$F$_5$)$_3$}$_2$] and [Se{Au$_2$(*m*-dppf)}{Au(C$_6$F$_5$)$_3$}] [18]; where dppf = (1,1′-bis(diphenylphosphino) ferrocene). The reported experimental distances for Au(I)–Au(III) centers are 341.2 and 372 pm, respectively, indicating the presence of weak interactions in these complexes. Also, quasi-relativistic (QR) pseudopotential (PP) calculations on [Se(AuPH$_3$)$_2$(AuR$_3$)], [Se(AuPH$_3$)(AuR$_3$)$_2$]$^-$ (R = –H, –CH$_3$), and [{Se(AuPH$_3$)}$_2${Au(CH$_3$)$_2$}$_2$] models have been performed at HF and MP2 levels. The results showed good agreement between the experimental and theoretical geometries at the MP2 level [18]. Moreover, Schwerdtfeger and co-workers [19] recently studied both the stability and the structure of *cis/trans*-(diphosphino)ethylene digold(I) halides. The authors found that the aurophilic interactions present in the *cis*-

isomer stabilize such compounds with respect to the *trans*-isomer to an extent which can only be calculated at the MP2 level through the double bond of the ethylene.

In the present work, we carried out an ab initio theoretical study on simplified models of the real complex [P(CH$_3$)$_3$Au(I)C(CF$_3$)=C(CF$_3$)Au(III) (CH$_3$)$_2$P(CH$_3$)$_3$]. Our aim was to determine the Au(I)–Au(III) distance and to estimate the strength of this interaction between Au(I) and Au(III) species. For this purpose, we used quasi-relativistic pseudopotential (QR-PP) calculations at both HF and MP2 levels. Also, we built two additional intermolecular models that allowed us to quantify the d^8–d^{10} interaction between both metallic centers.

2. Models and methods

2.1. Simplified models and theory

Several models of the experimental structure with the general formula [PH$_3$Au(I)C(L)=C(L) Au(III)(R)$_2$PH$_3$] used in our study are depicted in Fig. 1. The original trimethylphosphine and trifluoromethyl ligands were replaced by phosphine and the ligands L by a hydrogen atom and methyl groups according to the numbers given in that figure. In the present work, these simplified models were used to study the intramolecular d^8–d^{10} interaction between Au(I) and Au(III) centers for the *cis*- and *trans*-isomers numbered in Fig. 1 as compounds **1**, **3**, **5** and **2**, **4**, **6**, respectively. For compounds **1**–**2**, the ligands L and R are replaced by –H; for compounds **3**–**4**, L is replaced by –H and R by –CH$_3$, and finally for compounds **5**–**6** both ligands L and R are replaced by methyl groups. We first fully optimized the geometries for systems **1**–**6** at the HF and MP2 levels. We used these geometries to study the Au(I)–Au(III) intramolecular interactions.

Also, in order to estimate the intermolecular d^8–d^{10} interaction, we included two reduced models with the general formula [PH$_3$Au(I)R][PH$_3$ Au(III) (R)$_3$]. These compounds are showed in Fig. 1 as compounds **7** and **8**. The substituents are a hydrogen atom and a methyl group, respectively. Also, the monomers **7** and **8** have been full optimized.
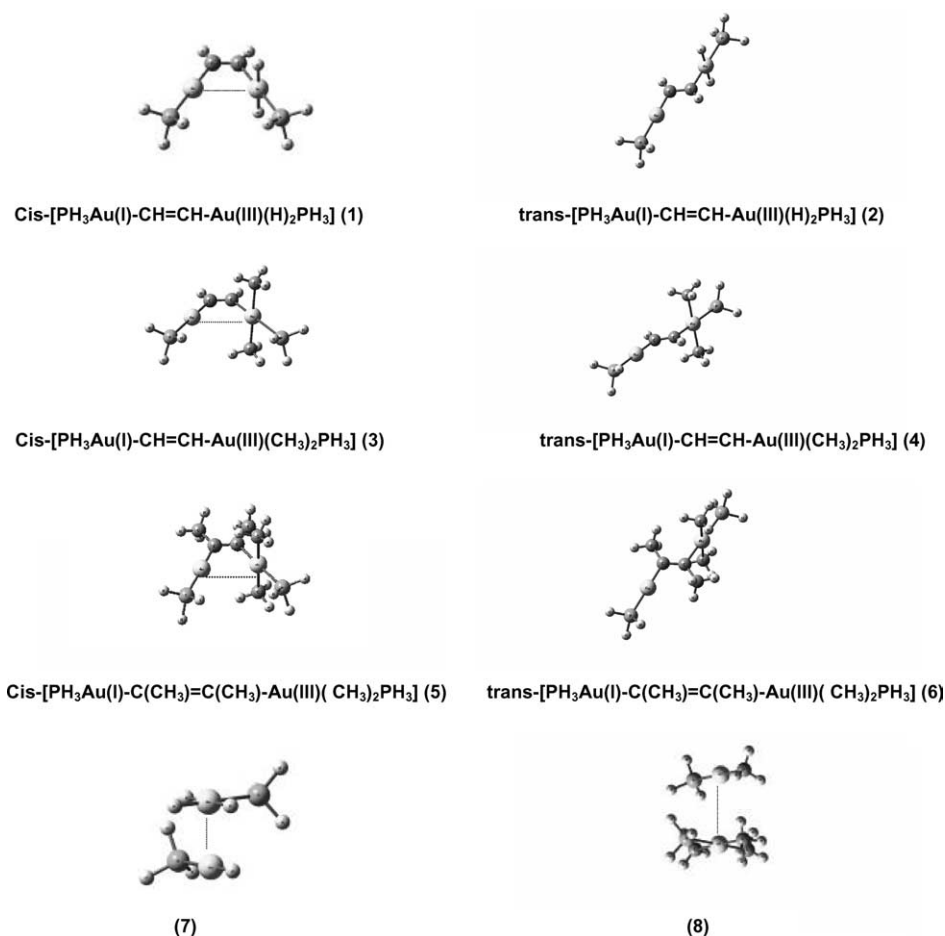
Cis-[PH$_3$Au(I)-CH=CH-Au(III)(H)$_2$PH$_3$] (1)

trans-[PH$_3$Au(I)-CH=CH-Au(III)(H)$_2$PH$_3$] (2)

Cis-[PH$_3$Au(I)-CH=CH-Au(III)(CH$_3$)$_2$PH$_3$] (3)

trans-[PH$_3$Au(I)-CH=CH-Au(III)(CH$_3$)$_2$PH$_3$] (4)

Cis-[PH$_3$Au(I)-C(CH$_3$)=C(CH$_3$)-Au(III)(CH$_3$)$_2$PH$_3$] (5)

trans-[PH$_3$Au(I)-C(CH$_3$)=C(CH$_3$)-Au(III)(CH$_3$)$_2$PH$_3$] (6)

(7)

(8)

Fig. 1. The intramolecular interaction models **1–6** with *cis-* and *trans-*isomers. The intermolecular interaction model **7–8**.

It is well known that the nature of intra- and intermetallic interactions for a given system can be studied by comparing HF and MP2 calculations [6,8]. Thus, when dispersion interactions are present in a system and if electronic correlation effects are included, a decrease in the calculate distance between metal centers is found when comparing HF and MP2 results. This has been reported by Pyykkö et al. [20] and Papadopoulos et al. [21] in systems with weak chemical interactions (hydrogen-bonded and aurophilic attractions). Although it is acknowledged that the MP2 approximation exaggerates attractive interactions, it gives a good indication of their existence [9]. Of course, a more accurate method would be CCSD(T) (coupled cluster single,

double and triple excitations), but it has the disadvantage that it is time consuming for the study of systems such as the proposed models **1–6**.

The interaction energy $V(R)$ for studying the Au(I)–Au(III) intermolecular interactions in the systems **7–8** was obtained according to Eq. (1). The counterpoise correction for the basis set superposition error (BSSE) on $\Delta E(R)$ was included.

$$\Delta E = E_{AB}^{(AB)} - E_A^{(AB)} - E_B^{(AB)} = V(R). \tag{1}$$

2.2. GAUSSIAN 98 calculations

The calculations were done using the GAUSSIAN 98 package [22]. For Au, the 19 valence-

Table 1
Basis sets and pseudopotentials (PPs) used in this work

Atom	PP	Basis	Exponents of polarization functions	Refs.
H	–	(4s1p)/[2s1p]	$\alpha_p = 0.80$	[23]
C	Bergner	(4s4p1d)/[2s2p1d]	$\alpha_d = 0.80$	[22]
P	Bergner	(4s4p1d)/[2s2p1d]	$\alpha_d = 0.34$	[22]
Au	Schwerdtfeger (QR) [1f]	(8s6p5d1f)/[6s5p3d1f]	$\alpha_f = 0.20$	[21]
Au	Schwerdtfeger (QR) [2f]	(8s6p5d2f)/[6s5p3d2f]	$\alpha_f = 0.20, 1.19$	[21]

electron (VE) quasi-relativistic (QR) pseudo-potential (PP) of Schwerdtfeger et al. [23] was employed. Consideration of f orbitals is necessary when studying weak inter- and intramolecular interactions, as it has been demonstrated previously for this atom [8,9]. We employed two f-type polarization functions for a more accurate description of the interaction energy. The diffuse f orbital exponent (0.20) was obtained by maximizing the Au(I) cation MP2 electric dipole polarizability and the compact f (1.19) by minimizing the CCSD(T) total energy of the Au(0) atom [8] (see Table 1).

The C and P atoms were treated through PPs, using double-zeta basis sets with the addition of one d-type polarization function [24]. For the H atom, a double-zeta basis set plus one p-type polarization function was used [25].

3. Results and discussion

3.1. Intramolecular interaction

Table 2 reports the optimized distances in pm obtained for models **1**–**6** at the HF and MP2 levels. It also shows the effect of the basis set on Au when one or two f polarization functions are used in both calculations. In the *trans*-models, only slight changes in the Au(I)–Au(III) distances are observed due to the fact that such centers are far away. On the other hand, for the *cis*-isomers (compounds **1**, **3**, **5**) it can be seen that at the HF level there is only little variation in the Au(I)–Au(III) distances, using either one or two f-polarization functions (values ranging from 377.3 to 379.8 pm); however, at the MP2 level, a greater variation can be appreciated. The effect of the L group on the Au(I)–Au(III) distances in the

models can also be accounted for, as it decreases when H is replaced by –CH$_3$ in the isomers. The Au(I)–Au(III) distances obtained decrease from 309.5 to 306.7 pm and 295.3 pm for the *cis* compounds **1**, **3**, **5**, respectively, when the MP2/2f calculations are compared. This result shows an inductive effect in these cases. Thus, using this methodology, the effect of the basis set with PPs on Au can be observed clearly. In fact, the best results are obtained when Au is modeled with two f polarization functions, where the distances are significantly shortened becoming comparable (although this shortening is smaller in magnitude compared with the experimental data, see *cis*-isomer in Table 2). However, it is worth noting that the MP2 approximation overestimates the attraction. Despite of this, our results clearly evidence aurophilic interactions at this level.

In terms of the total energy obtained when pair of *cis*-**1** and *trans*-**2** isomers are compared, despite the stabilizing effect when two f-polarization functions are used in the calculations, the *trans*-isomers are always more stable at the HF level. This is due to the fact that this methodology is unable to describe accurately the interaction between Au(I) and Au(III). However, this situation is reverted when post-HF calculations are carried out on these systems. Thus, carrying out MP2 calculations makes it possible to estimate the contribution of the electronic correlation to the intramolecular contacts and to recognize the real effect of the latter in these systems.

By comparing the differences in the relative energies between the *cis*- and *trans*-structures, denoted by $\Delta E(cis/trans)$ in kJ mol^{-1} in Table 3, obtained using both methodologies, it is possible to account for the greater stability of the *cis*-isomer at the MP2 level. Again, there is good agreement with

Table 2
Main geometric parameters of the models studied with both basis sets by Au[a,b]

System	Isomer	Method	Au(I)–Au(III)	Au(I)–C	Au(III)–C	C=C
[PH$_3$AuCH=CHAu(H)$_2$ PH$_3$]	cis-**1**	HF/1f	379.8	208.1	205.1	131.5
		MP2/1f	320.6	202.9	204.9	134.5
		HF/2f	379.2	207.3	204.0	131.9
		MP2/2f	309.5	199.8	202.4	134.6
	trans-(**2**)	HF/1f	497.9	208.1	205.6	132.0
		MP2/1f	490.8	203.1	205.8	134.6
		HF/2f	498.4	207.3	204.7	132.2
		MP2/2f	487.9	199.8	203.1	134.6
[PH$_3$AuCH=CHAu(CH$_3$)$_2$ PH$_3$]	cis-**3**	HF/1f	378.8	208.2	202.8	131.9
		MP2/1f	316.9	202.8	202.9	134.8
		HF/2f	379.3	207.6	202.2	132.0
		MP2/2f	306.7	200.3	200.9	134.8
	trans-**4**	HF/1f	497.9	208.2	203.5	132.1
		MP2/1f	490.7	202.7	203.3	134.9
		HF/2f	496.9	207.6	202.8	132.2
		MP2/2f	486.3	200.1	201.3	134.8
[PH$_3$AuCCH$_3$=CCH$_3$ Au(CH$_3$)$_2$PH$_3$]	cis-**5**	HF/1f	378.3	208.3	205.9	131.6
		MP2/1f	300.3	201.8	203.7	134.9
		HF/2f	377.3	208.9	205.3	132.6
		MP2/2f	295.3	200.7	202.9	134.8
	trans-**6**	HF/1f	499.5	209.6	207.3	132.1
		MP2/1f	484.7	201.9	204.3	134.2
		HF/2f	498.8	210.1	206.5	132.2
		MP2/2f	482.9	200.9	203.3	134.4
[P(CH$_3$)$_3$Au(I)C(CF$_3$)=C(CF$_3$) Au(III)(CH$_3$)$_2$P(CH$_3$)$_3$]	cis-	Experiment	331.0	210.0	203.0	128.0

[a] 1f with $\alpha_f = 0.2$.
[b] 2f with $\alpha_f = 0.2, 1.19$.

the experimental evidence. As stated before, at the HF level, in all models, the *trans*-isomers are the more stable ones. It can also be seen that adding a second f polarization function only increases the energy difference between the *cis*- and *trans*-structures at the MP2 level.

Another estimate of the aurophilic attraction energy uses the operational definition given by Pyykkö and Tamm [26]: 'the difference between the MP2 energies of a system at Hartree–Fock and MP2 optimized geometries, respectively, divided by the number of Au–Au interactions present in the system (N)'. In our case $N = 1$ and we use:

$$\Delta E = E_{HF\ geometry}^{(MP2)} - E_{MP2\ geometry}^{(MP2)}. \quad (2)$$

Table 3
The energy difference between the *cis* and *trans* models (in kJ mol^{-1})

System	Method	$\Delta E(cis/trans)$
[PH$_3$AuCH=CHAu(H)$_2$PH$_3$]	HF/1f	−16.20
	MP2/1f	2.34
	HF/2f	−16.35
	MP2/2f	7.98
[PH$_3$AuCH=CHAu(CH$_3$)$_2$ PH$_3$]	HF/1f	−13.78
	MP2/1f	10.94
	HF/2f	−13.52
	MP2/2f	22.94
[PH$_3$AuC(CH$_3$)=C(CH$_3$) Au(CH$_3$)$_2$PH$_3$]	HF/1f	−10.85
	MP2/1f	15.65
	HF/2f	−10.92
	MP2/2f	17.98

Table 4
Aurophilic interaction energies, ΔE in a.u. (kJ mol^{-1}), of the systems studied from Eq. (2)

System	Method	$\Delta E_{\text{HF geom.}}^{\text{MP2}}$	$\Delta E_{\text{MP2}}^{\text{MP2}}$	ΔE
cis-[PH$_3$AuCH=CHAu(H)$_2$PH$_3$]	1f	−300.39573	−300.40344	0.00771 (20.2)
	2f	−300.93347	−300.94454	0.01107 (29.1)
cis-[PH$_3$AuCH=CHAu(CH$_3$)$_2$PH$_3$]	1f	−314.04471	−314.05586	0.01115 (29.3)
	2f	−314.57834	−314.59237	0.01403 (36.8)
cis-[PH$_3$AuC(CH$_3$)=C(CH$_3$)Au(CH$_3$)$_2$PH$_3$]	1f	−327.72602	−327.73457	0.00855 (22.5)
	2f	−328.26048	−328.27247	0.01199 (31.5)

The total energies of the systems in a.u.

Table 5
NBO analysis at the HF/2f and MP2/2f levels for *cis/trans*-isomers

System	Atom	*cis*-HF	*cis*-MP2	*trans*-HF	*trans*-MP2
cis-[PH$_3$AuCH=CHAu(H)$_2$PH$_3$]	Au(I)	+0.316	+0.169	+0.319	+0.179
	Au(III)	+0.762	+0.560	+0.755	+0.577
	C^a	−0.621	−0.548	−0.616	−0.550
	C^b	−0.366	−0.347	−0.364	−0.349
	P^a	+0.192	+0.171	+0.190	+0.163
	P^b	+0.229	+0.202	+0.226	+0.194
cis-[PH$_3$AuCH=CHAu(CH$_3$)$_2$PH$_3$]	Au(I)	+0.319	+0.183	+0.329	+0.186
	Au(III)	+0.927	+0.710	+0.925	+0.730
	C^a	−0.614	−0.553	−0.615	−0.558
	C^b	−0.354	−0.346	−0.352	−0.351
	P^a	+0.198	+0.177	+0.198	0.171
	P^b	+0.219	+0.211	+0.216	+0.203
cis-[PH$_3$AuC(CH$_3$)=C(CH$_3$)Au(CH$_3$)$_2$PH$_3$]	Au(I)	+0.341	+0.342	+0.332	+0.326
	Au(III)	+0.923	+0.911	+0.911	+0.918
	C^a	−0.515	−0.504	−0.504	−0.505
	C^b	−0.254	−0.257	−0.261	−0.253
	P^a	+0.225	+0.229	+0.222	+0.223
	P^b	+0.268	+0.268	+0.266	+0.265

[a] C and P bond at Au(I).
[b] C and P bond at Au(III).

Table 6
NBO electron configuration at the HF/2f and MP2/2f levels for Au(I) and Au(III) in isomer of [PH$_3$AuC(CH$_3$)=C(CH$_3$)Au(CH$_3$)$_2$PH$_3$] (**5–6**)

System	Method	Atom	
[PH$_3$AuC(CH$_3$)=C(CH$_3$)Au(CH$_3$)$_2$PH$_3$]	*cis*-HF	Au(I)	$6s^{0.89}5d^{9.75}6p^{0.01}$
		Au(III)	$6s^{0.66}5d^{9.38}6d^{0.02}7p^{0.01}$
	cis-MP2	Au(I)	$6s^{0.89}5d^{9.74}6p^{0.01}7p^{0.01}$
		Au(III)	$6s^{0.66}5d^{9.38}6d^{0.02}7p^{0.01}$
	trans-HF	Au(I)	$6s^{0.89}5d^{9.76}6p^{0.01}$
		Au(III)	$6s^{0.66}5d^{9.39}6d^{0.02}$
	trans-MP2	A(I)	$6s^{0.91}5d^{9.75}6p^{0.01}$
		Au(III)	$6s^{0.66}5d^{9.38}6d^{0.02}$

The results are shown in Table 4. The energy of the system is relaxed on going from the HF geometry to the MP2 geometry, giving an approximation to the intramolecular aurophilic attraction. The incorporation of a second f function on the gold atoms stresses the interaction energy. In general, the values reported in Table 4 are in range reported for aurophilic interactions [8,9].

The MP2 calculations are able to reproduce the structural trends found in the experimental complexes. Before proceeding, we would like to compare the charges obtained from the natural bond orbital (NBO) [27] population at the HF and MP2 levels (data shown in Table 5). The data show in all the models a reduction in the formal oxidation state of the atoms on going from HF to MP2, as well as on going from the *cis*- to the *trans*-isomer. The charges on the Au(I) and Au(III) atoms at the MP2 level are smaller when the groups L and R are –H rather than the –CH$_3$ group. If we compare the charges on Au(I) and Au(III) between the *cis*- and *trans*-isomers, at the same level of theory, we find slightly smaller value for the *cis*-isomers. However, this is not sufficient to justify the greater stability of the *cis*-models at the MP2 level.

Furthermore, we have included the electron configuration for Au(I) and Au(III) obtained in the model [PH$_3$AuC(CH$_3$)=C(CH$_3$)Au(CH$_3$)$_2$PH$_3$] (**5–6**) at the HF and MP2 levels (see Table 6). There

are no relevant changes on going from the *cis*- to the *trans*-isomer and from HF to MP2. This situation is maintained for the other two models (not shown here).

3.2. Intermolecular interaction

In order to estimate the Au(I)–Au(III) interaction, we built two ideal intermolecular models (see Fig. 1, models **7–8**). The results are summarized in Fig. 2. The interaction potential, $V(R)$, was calculated from Eq. (1). The effects of the L groups, namely –H and –CH$_3$, on the $V(R)$ are attractive at the MP2 level but repulsive at the HF level. The trimethylated dimer (compound **8**) gives a flat minimum. The interaction energies at equilibrium distances (R_e) are −24.29 and −21.72 kJ mol^{-1} for models **7** and **8**, respectively. The calculated interaction energy for model **8** is 15% lower than that calculated for model **7**, and the equilibrium distance increases from 325 pm when L = –H to 373 pm for L = –CH$_3$. Such a difference may be due to the steric effects of the –CH$_3$ groups. Thus, the calculated interaction between both Au ions with d^8–d^{10} configurations is around 21–25 kJ mol^{-1}, which is in fact a typical value reported for the metallophilic attraction [6]. If we compare these results with the ones in Table 4, it is possible to appreciate they have the same magnitude.
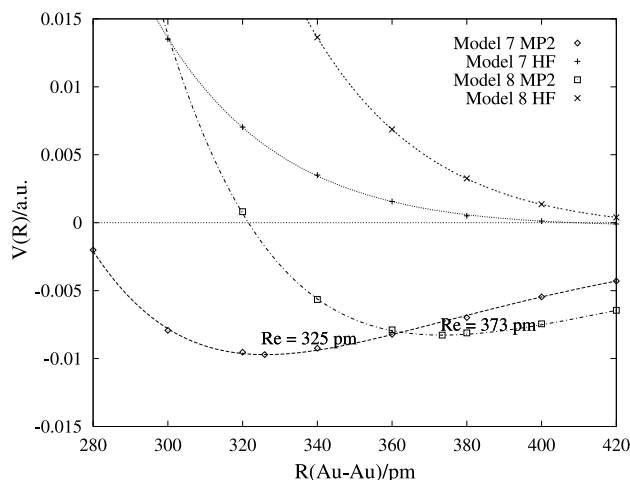

Fig. 2. HF and MP2 interaction energies for the dimer as function of the Au(I)–Au(III) distance, R, for models **7–8**.

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