Theoretical study of the aggregation of d^{10}–s^2 Au(I)–Tl(I) complexes in extended unsupported chains

Eduardo J. Fernández [a], Antonio Laguna [b,*], José M. López-de-Luzuriaga [a],
Miguel Monge [a], Fernando Mendizabal [c,*]

[a] *Departamento de Química, Universidad de la Rioja, Grupo de Síntesis Química de La Rioja, UA-CSIC,
Complejo Científico Tecnológico, 26001 Logroño, Spain*
[b] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain*
[c] *Departamento de Química, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile*

Abstract

Model compounds are used to study the metallophilic attraction between gold and thallium atoms. Ab initio calculations on dimers and tetramers in different distributions of the minimal units are analyzed. An attraction is found for all models and there is a reasonable agreement between the experimental and theoretical geometries at the HF and MP2 levels.

1. Introduction

In the last years the bonding interaction between closed-shell metal atoms have been widely studied from theoretical and experimental points of view [1,2]. Among the heavy metal atoms are the gold–gold interactions (aurophilicity) the ones which have received most attention. Also, in the last times it can be found in the literature gold(I)-containing heterometallic systems in which short closed-shell metal–metal interactions are present (metallophilicity) [3–6]. Thus, for example, Au^I–Pd^{II} (d^{10}–d^8) [7], Au^I–Ag^I (d^{10}–d^{10}) [8], Au^I–Cu^I (d^{10}–d^{10}) [8] and Au^I–Tl^I (d^{10}–s^2) [9–11] interactions have been theoretically described using correlated methods and it has been shown that the metallophilic interactions arise from dispersion-type correlation effects (van der Waals) and charge transfer contributions [11].

The formation of Au–M interactions based on acid–base reactions like, for instance, Tl^+ or Ag^+ Lewis acids precursors with $[AuR_2]^-$ ($R = C_6F_5$ or C_6Cl_5) Lewis bases, provides an additional electrostatic attraction [12]. On the other hand, some of these Au^I–metal complexes have been revealed as a new class of photoluminescent materials in which the emission of radiation results mainly from the interactions between the different metal centres [13].

We have succeeded in the synthesis of Au–Tl complexes through the use of $[AuR_2]^-$ Lewis base precursors against Tl^+ salts acting as Lewis acids [9–11]. Thus, we have reported the synthesis and luminescent behaviour of the first unsupported gold–thallium chain [Tl(OPPh₃)₂][Au(C₆F₅)₂] [11] and new two- and three-dimensional arrays of the type [Tl(4,4′-bipy)ₙ][AuR₂] ($R = C_6F_5$ and C_6Cl_5; 4,4′-bipy = 4,4′-bipyridine) [12], in which the change of the perhalophenyl ligands gives rise to different structural arrangements. From a theoretical point of view, the metallophilicity between gold(I) and thallium(I) centres in these compounds gives an average metal–metal

* Corresponding authors. Tel.: +56 2 9787397; fax: +56 2 2713888.
 E-mail addresses: alaguna@unizar.es (A. Laguna), hagua@uchile.cl (F. Mendizabal).

separation of 300 pm and the interaction energy is estimated at about 276 kJ/mol, of which 80% are of an ionic origin [11].

When examining the details of the supramolecular chemistry of the [Tl(bipy)$_2$][Au(C$_6$F$_5$)$_2$]$_2$ [12] in the solid state, the complex consists of a planar polymer arrangement formed by a Tl–Au–Au–Tl metal disposition following the pattern [+−−+] for the fragment charges. This situation is at variance with the simple rules of Coulomb forces. While under certain experimental conditions, it is possible to obtain the common pattern [−+−+] and [−++−] [21].

In this paper we report ab initio calculations at Hartree–Fock (HF) and Møller–Plesset (MP2) levels of theory on simplified model systems using quasi-relativistic effective core potentials in order to study the nature of the d^{10}–s^2 Au$^I\cdots$Tl^I interaction for di- and tetra-nuclear species. This permitted us to understand the forces that operate in the building up of the supramolecular arrangements in the solid state.

2. Models and computational details

The Gaussian 03 package [14] was used. The following basis sets and pseudopotentials (PP) were used: the 19-valence electron (VE) and 3-VR quasi-relativistic (QR) pseudopotential (PP) were employed for gold and thallium, respectively [15,16]. We have employed two f-type polarization functions for Au and Tl centres. The f orbitals are necessary for the weak intermolecular interactions, as was demonstrated previously for various metals [8,11]. Carbon and nitrogen atoms were also treated by Stuttgart pseudopotentials [17], including only the valence electrons for each atom. For carbon and nitrogen atoms, double-zeta basis sets were used, augmented by d-type polarization functions; for the H atom, a double-zeta plus one p-type polarization function was used [18].

First, we studied the experimental compounds through the model [Tl(bipy)$_2$][Au(C$_6$H$_5$)$_2$]. We replaced the groups –C$_6$F$_5$ by –C$_6$H$_5$. We optimized the structures [Tl(bipy)$_2$]$^+$
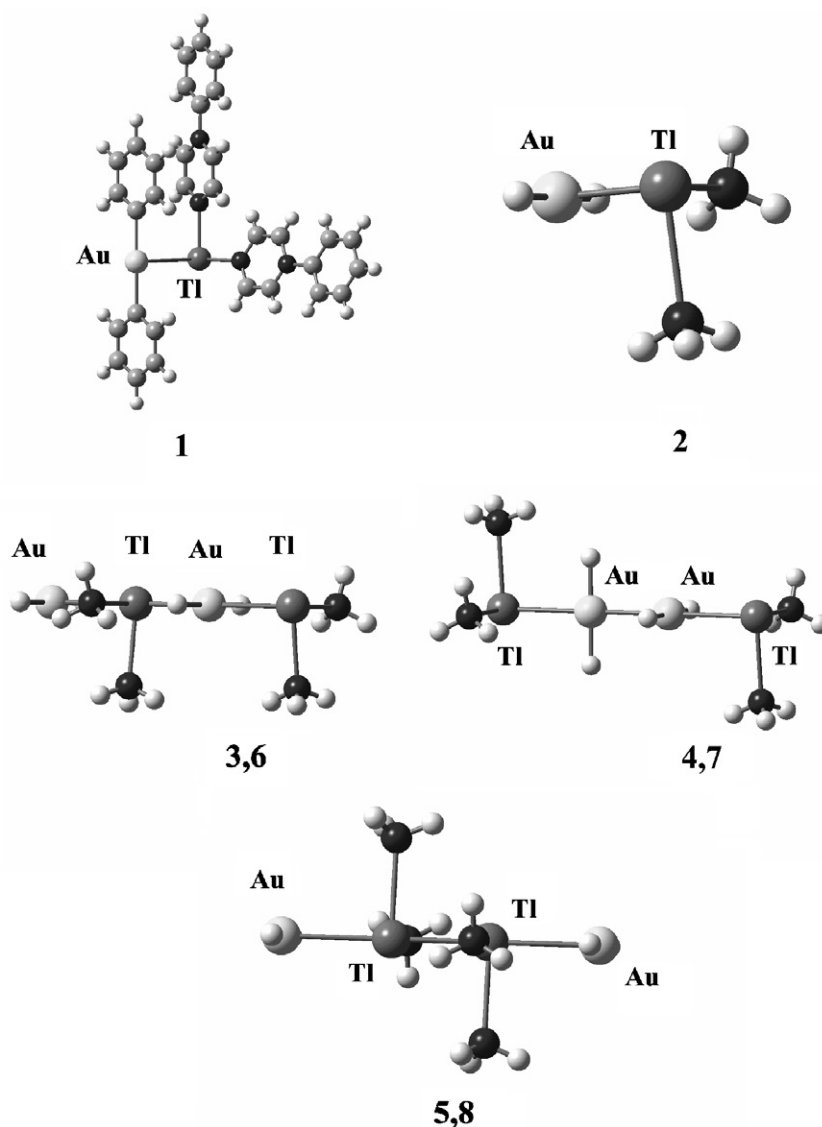

Fig. 1. Theoretical model systems.

and $[Au(C_6H_5)_2]^-$ separately at second-order Møller–Plesset perturbation theory (MP2) level (see Fig. 1). Due to the fact that the size of the system is large (tetra-nuclear model), we propose a reduced system. Thus, we replaced $[Tl(bipy)_2]^+$ and $[Au(C_6H_5)_2]^-$ by $[Tl(NH_3)_2]^+$ and $[AuH_2]^-$. This will permit to study the tetra-nuclear species. At a first instance it gives the impression of being a very coarse replacement. However, we wait to find with these results an approximation to the effects that operate in the real system.

We studied the intermolecular interactions by comparing the Au–Tl distances obtained at HF and MP2 levels. The counterpoise correction for the basis-set superposition error (BSSE) was used for the interaction energies calculated. We have fully optimized the geometry of the model for each one of the methods mentioned above. Although it is known that the MP2 approximation exaggerates the attractive interactions, this method gives a good indication of the existence of some type of interaction [19,20].

3. Results and discussion

The geometries of the fragments were fully optimized at MP2 level of theory. A C_{2v} point symmetry was assumed for the thallium fragment, while a D_{2h} and $D_{2\infty}$ symmetries were used for the gold anion fragments. The optimized geometries (distances and angles) are given in Table 1 for some parameters. The structural data are in the experimental range [12].

We have described the experimental structures through idealized dimer models $[Au(C_6H_5)_2]$–$[Tl(bipy)_2]$ (**1**) and $[AuH_2]$–$[Tl(NH_3)_2]$ (**2**) (Fig. 1) with a C_{2v} symmetry. In Table 2 we summarize the Au–Tl interaction energies and equilibrium distances. The calculated distances fall in the same range as the experimental ones. Using quasi-relativistic pseudopotentials, the Au–Tl distance at HF is larger than the one obtained at MP2 level, the latter being very closed to the experimental values for the model **1**. The model **2** tends to shorten the distance Au–Tl due to the simplified nature of the model. The energy magnitudes at HF and MP2 levels are in the electrostatic interaction range. Fig. 2 shows the potential energy curves for both models. The energetic difference between HF and MP2 are 70.9 kJ/mol and 40.7, respectively, for models **1** and **2**. This magnitude is within the range of the dispersion-type van der Waals interactions with charge transfer.

The MP2 calculation is able to reproduce the structural trends found in the experimental data. On the other hand, the interaction energy at MP2 level is composed by 80% and 90% of ionic interaction, 20% and 10% of van der Waals interactions for models **1** and **2**, respectively. It is assumed that the electrostatic interaction is responsible for the attractive behaviour obtained at HF level and that the additional stabilization obtained at the MP2 level is due to the introduction of dispersion-type correlation effects and charge transfer contributions. We can conclude that model **2** describes well the behaviour observed for the metallophilic Au–Tl attraction. Thus, it can be used to describe more complex systems as the tetra-nuclear ones.

We have built two groups of linear tetramer units. The first group is built up through the interaction between
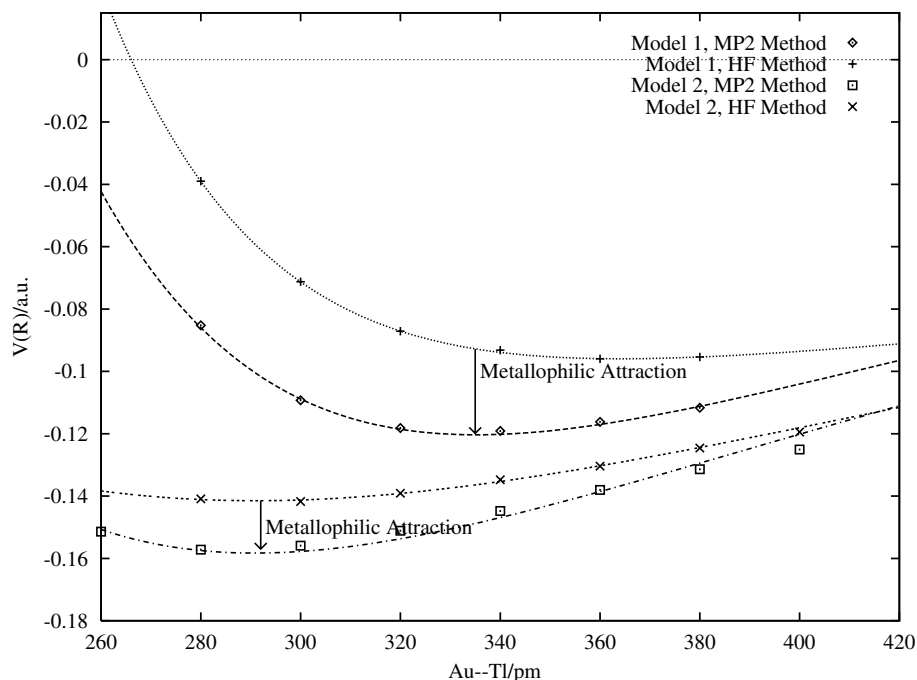
Table 1
Main geometric parameters of the monomer systems at MP2 level (distances in pm and angles in degrees)

Monomer system	Au–L	Tl–N	L–Au–L	N–Tl–N
$[Au(C_6H_5)_2]^-$	206.9		180.0°	
$[AuH_2]^-$	166.4		180.0°	
$[Tl(bipy)_2]^+$		256.9		96.8°
$[Tl(NH_3)_2]^+$		268.9		83.2°

Table 2
Optimized Tl–Au distance, R_e, for the models at the MP2 and HF levels

Model system	Method	R_e	$V(R_e)$	ΔE(MP2–HF)[a]
$[Au(C_6H_5)_2]$–$[Tl(bipy)_2]$ (**1**)	MP2	335.4	−314.7	−70.9
	HF	364.0	−251.9	
$[AuH_2]$–$[Tl(NH_3)_2]$ (**2**)	MP2	291.9	−412.1	−40.7
	HF	290.9	−371.4	
$[Tl(NH_3)_2][AuH_2]$–$[Tl(NH_3)_2][AuH_2]$ (**3**)	MP2	327.6	−33.66	−27.4
	HF	367.7	−10.9	
$[Tl(NH_3)_2][AuH_2]$–$[AuH_2][Tl(NH_3)_2]$ (**4**)	MP2	276.3	−26.8	−66.9
	HF	[b]		
$[AuH_2][Tl(NH_3)_2]$–$[Tl(NH_3)_2][AuH_2]$ (**5**)	MP2	420.1	−11.2	−14.3
	HF	[b]		
$[Tl(NH_3)_2]$–$[AuH_2][Tl(NH_3)_2][AuH_2]$ (**6**)	MP2	284.4	−458.9	−50.1
	HF	292.8	−409.9	
$[Tl(NH_3)_2]$–$[AuH_2][AuH_2][Tl(NH_3)_2]$ (**7**)	MP2	279.3	−536.4	−46.8
	HF	285.7	−490.4	
$[AuH_2]$–$[Tl(NH_3)_2][Tl(NH_3)_2][AuH_2]$ (**8**)	MP2	283.3	−421.7	−42.1
	HF	292.5	−380.8	

Distance R_e in pm; interaction energy $V(R_e)$ in kJ/mol.
[a] MP2 equilibrium distance.
[b] Repulsive curve.

Fig. 2. HF and MP2 potential energy curves for [Au(C$_6$H$_5$)$_2$]–[Tl(bipy)$_2$] (**1**) and [AuH$_2$]–[Tl(NH$_3$)$_2$] (**2**).

two Au–Tl dimers (models **3**–**5**). The second group is constructed through the interaction of a fragment with a trimer (**6**–**8**). The Figs. 3 and 4 described the potential curves at HF and MP2 levels for the interactions. The results are summarized in Table 2.

Models **3**–**5** show a classic metallophillic interaction among the metallic atoms. In models **3** and **4** the distances

and interaction energies are found to be shorter and more stable than in system **5**. If we take into account the electronic correlation effects, the [+−−+] (**4**) system (66.9 kJ/mol) is found to be more stable followed by [+−+−] (**3**) (27.4 kJ/mol) and finally [−+−+] (**5**) (14.3 kJ/mol). A similar result is observed experimentally for the compound [Tl(bipy)$_2$][Au(C$_6$F$_5$)$_2$]$_2$ [14] with the sequence [+−−+].
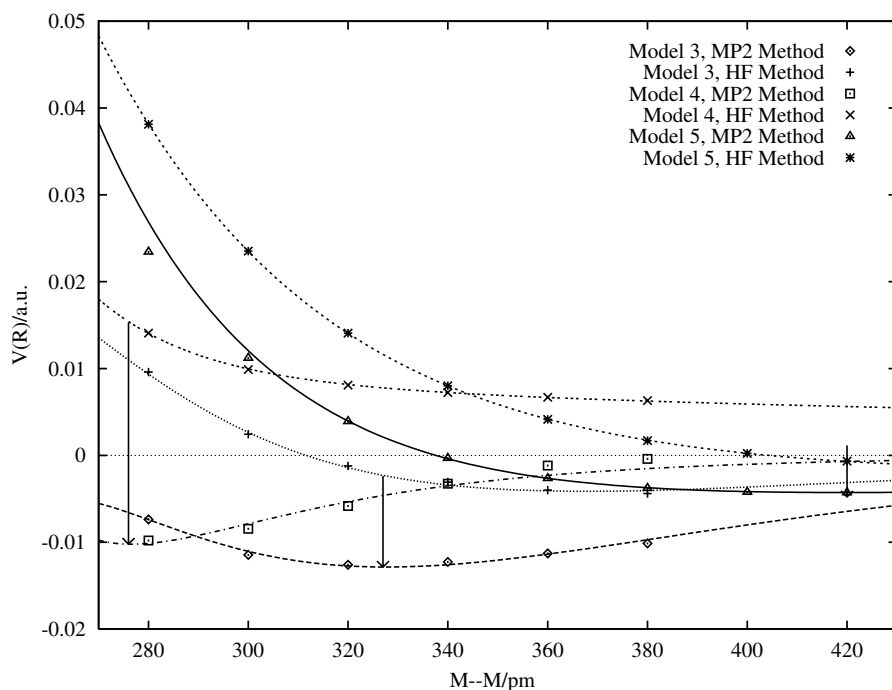
Fig. 3. HF and MP2 potential energy curves for [Tl(NH$_3$)$_2$][AuH$_2$]–[Tl(NH$_3$)$_2$][AuH$_2$](**3**), [Tl(NH$_3$)$_2$][AuH$_2$]–[AuH$_2$][Tl(NH$_3$)$_2$] (**4**), and [AuH$_2$][Tl(NH$_3$)$_2$]–[Tl(NH$_3$)$_2$] [AuH$_2$] (**5**).
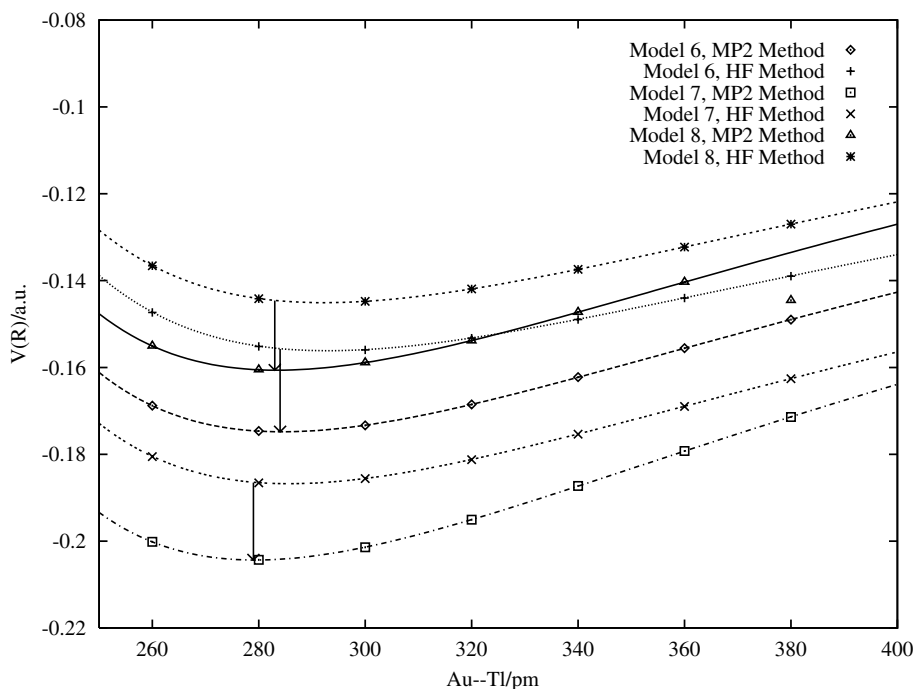
Fig. 4. HF and MP2 potential energy curves for $[Tl(NH_3)_2]–[AuH_2][Tl(NH_3)_2][AuH_2]$ (**6**), $[Tl(NH_3)_2]–[AuH_2][AuH_2][Tl(NH_3)_2]$ (**7**), and $[AuH_2]–[Tl(NH_3)_2]–[Tl(NH_3)_2][AuH_2]$ (**8**).

Table 3
NBO Charge on Au and Tl in the models at MP2 level

Model system	Metal	Metal	Metal	Metal
$[Au(C_6H_5)_2]–[Tl(bipy)_2]$ (**1**)	+0.401	+0.802		
$[AuH_2]–[Tl(NH_3)_2]$ (**2**)	+0.177	+0.732		
$[Tl(NH_3)_2][AuH_2]–[Tl(NH_3)_2][AuH_2]$ (**3**)	+0.732	+0.156	+0.717	+0.179
$[Tl(NH_3)_2][AuH_2]–[AuH_2][Tl(NH_3)_2]$ (**4**)	+0.693	+0.181	+0.181	+0.693
$[AuH_2][Tl(NH_3)_2]–[Tl(NH_3)_2][AuH_2]$ (**5**)	+0.188	+0.703	+0.703	+0.188

An analogous result was found by Pyykkö and co-worker for the system $\{[(H_3P)_2Au]^+[AuCl_2]^-\}_2$ achieving to reproduce a pattern $[+--+]$ [21].

If we focused on the natural bond orbital (NBO) population of Au, Tl and the fragments, it is easier to understand the ionic effects on the different models (Table 3). The data show in all the models a reduction of the formal oxidation state for gold and thallium. The smaller charge is found at gold in the calculated models, while a larger positive charge is concentrated at the thallium centers. However, in all the models, we find the same magnitude of charge on the metallic atoms, which would give rise to a repulsive interaction. The total charge on the fragments is of opposite size, what permits the Coulomb interaction. Model **4** shows the smaller repulsion among the neighbouring metal centers.

In the second group of models used (**6–8**) we study the growth effect of the polymer through the interaction between a monomer and a trimer. Both systems are charged, thus the main interaction will be of ionic type (Coulomb). This can be observed in Table 2 and Fig. 4. If we take into account the electronic correlation effects, all systems are stabilized in a similar amount of energy (ΔE(MP2–HF)). It is the ionic term the one that displays the difference. The most stable situation is found for the $[+--+]$ (**7**) system followed by $[+-+-]$ (**6**) and finally $[-+-+]$ (**8**). It is the same trend found for models **3–5**.

4. Conclusions

The present study provides further information about to the nature of the interactions in the Au–Tl in tetra-nuclear models. We found that the interactions are due to electronic correlation and ionic effects. Both effects are important when we consider the training of the polymer from smaller units. The most stable energy is found for the $[+--+]$ pattern, analogous to the experimental arrangement.

References

[1] P. Pyykkö, Chem. Rev. 97 (1997) 597.

[2] H. Schmidbaur, Gold Bull. 23 (1990) 11;
H. Schmidbaur, Gold Bull. 33 (2000) 1.

[3] L.H. Gade, Angew. Chem. 109 (1997) 1219;
L.H. Gade, Angew. Chem. Int. Ed. Engl. 36 (1997) 1171.

[4] F. Mendizabal, G. Zapata-Torres, C. Olea-Azar, Chem. Phys. Lett. 412 (2005) 477.

[5] E.J. Fernández, M.C. Gimeno, A. Laguna, J.M. López-de-Luzuriaga, M. Monge, P. Pyykkö, D. Sundholm, J. Am. Chem. Soc. 122 (2000) 7287.

[6] O. Crespo, E.J. Fernández, P.G. Jones, A. Laguna, J.M. López-de-Luzuriaga, A. Mendía, M. Monge, M.E. Olmos, Chem. Commun. (1998) 2233.

[7] O. Crespo, A. Laguna, E.J. Fernández, J.M. López-de-Luzuriaga, P.G. Jones, M. Teichert, M. Monge, P. Pyykkö, N. Runeberg, M. Schütz, H.-J. Werner, Inorg. Chem. 39 (2000) 4786.

[8] P. Pyykkö, N. Runeberg, F. Mendizabal, Chem. Eur. J. 3 (1997) 1451;
E.J. Fernández, J.M. López-de-Luzuriaga, O. Crespo, A. Laguna, P.G. Jones, M. Monge, P. Pyykkö, N. Runeberg, Eur. J. Inorg. Chem. (2002) 750.

[9] E.J. Fernández, A. Laguna, J.M. López-de-Luzuriaga. M. Monge, M. Montiel, M.E. Olmos, Inorg. Chem. 46 (2007) 2953.

[10] M. Bardají, A. Laguna, Eur. J. Inorg. Chem. (2003) 3069.

[11] E.J. Fernández, P.G. Jones, A. Laguna, J.M. López-de-Luzuriaga, F. Mendizabal, M. Monge, M.E. Olmos, J. Pérez, Chem. Eur. J. 9 (2003) 456.

[12] E.J. Fernández, P.G. Jones, A. Laguna, J.M. López-de-Luzuriaga, M. Monge, M.E. Olmos, J. Pérez, Inorg. Chem. 41 (2002) 1056.

[13] E.J. Fernández, A. Laguna, J.M. López-de-Luzuriaga, Coord. Chem. Rev. 249 (2005) 1423.

[14] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, K.T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Gaussian, Inc., Pittsburgh, PA, USA, 2003.

[15] P. Schwerdtfeger, M. Dolg, W.H.E. Schwarz, G.A. Bowmaker, P.D.W. Boyd, J. Chem. Phys. 91 (1989) 1762.

[16] W. Kuechle, M. Dolg, H. Stoll, H. Preuss, Mol. Phys. 74 (1991) 1245.

[17] A. Bergner, M. Dolg, W. Küchle, H. Stoll, H. Preuss, Mol. Phys. 80 (1993) 1431.

[18] T.H. Dunning, P.J. Hay, in: H.F. Schaefer (Ed.), Modern Theoretical Chemistry, vol. 3, Plenum Press, New York, 1997, pp. 1–28.

[19] P. Pyykkö, F. Mendizabal, Inorg. Chem. 37 (1998) 3018.

[20] N. Runeberg, M. Schütz, H.-J. Werner, J. Chem. Phys. 110 (1999) 7210.

[21] P. Pyykkö, W. Schneider, A. Bauer, A. Bayler, H. Schmidbaur, Chem. Commun. (1997) 1111.