

Theoretical study of the interaction $d^{10}-s^2$ between Pt(0) and Tl(I) on the $[\text{Pt}(\text{PH}_3)_3\text{Tl}]^+$ complex

Fernando Mendizabal ^{a,*}, Gerald Zapata-Torres ^b, Claudio Olea-Azar ^b

^a Departamento de Química, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile

^b Departamento de Química Inorgánica y Analítica, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Casilla 233, Santiago 1, Chile

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Abstract

We studied the attraction between $[\text{Pt}(\text{PH}_3)_3]$ and Tl(I) in the $[\text{Pt}(\text{PH}_3)_3\text{Tl}]^+$ complex using ab initio methodology. We found that the changes around the equilibrium distance Pt–Tl and in the interaction energies are sensitive to the electron correlation potential. This effect was evaluated using several levels of theory, including HF, MPn ($n = 2-4$), CCSD and CCSD(T). The obtained interaction energies differences at the equilibrium distance R_e (Pt–Tl) range from 134 to 205 kJ/mol at the different levels used. At long-distances, the behaviour of the $[\text{Pt}(\text{PH}_3)_3\text{Tl}]^+$ interaction may be related mainly to charge-induced dipole and dispersion terms, both involving the individual properties of $[\text{Pt}(\text{PH}_3)_3]$ and thallium ion. However, the charge-induced dipole term (R^{-4}) is found as the principal contribution in the stability at the long and short distances. The dispersion interaction is smaller, but not negligible near equilibrium distance.

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1. Introduction

The group of Catalano has synthesized and reported a series of compounds with bonding interactions in closed-shell systems between d^{10} Pt(0) or Pd(0) and s^2 ions such as Tl(I) or Pb(II) [1–4]. Some of these compounds were obtained by direct reaction of d^{10} -metallo-cryptands and ions or by reaction with coordinated compounds such as $[\text{Pt}(\text{PPh}_2\text{Py})_3]$ and Tl(I) ion. Catalano has indicated for the $[\text{Pt}(\text{PPh}_2\text{Py})_3\text{Tl}]^+$ complex: ‘the origin of this metallophilic attraction is not completely understood’. NMR studies in solution for compounds that contain ^{205}Tl and ^{195}Pt have been carried out in order to establish a high stability of this hetero-metallic bond [1].

Closed-shell interactions range from extremely weak van der Waals forces to metallophilic and extremely

strong s^2-s^2 interactions [5,6]. In fact, it is possible to find reports in the literature for diatomic systems with $d^{10}-s^2$ strong closed-shell interactions such as AuHg^+ and AuXe^+ with interaction energies of 179 and 87 kJ/mol, respectively [7–9]. In these systems, two complementary forces have been identified: charge-induced dipole (cid) and dispersion (disp) interactions [10].

The aim of the present work is to study theoretically the intermolecular interaction $d^{10}-s^2$ using the $[\text{Pt}(\text{PH}_3)_3\text{Tl}]^+$ complex as a model, comparing the Pt(0)–Tl(I) distances and estimating the strength of this interaction at the HF, MP2, MP3, MP4, CCSD and CCSD(T) levels by means of used scalar relativistic pseudopotentials (PPs). In addition, in order to estimate the nature of the intermolecular interactions, we have included two simple expressions: charge-induced dipole and dispersion, calculated from the individual properties of $[\text{Pt}(\text{PH}_3)_3]$ and Tl(I) at MP2 level [7,10].

* Corresponding author. Fax: +56 2271 3888.

E-mail address: hagua@uchile.cl (F. Mendizabal).

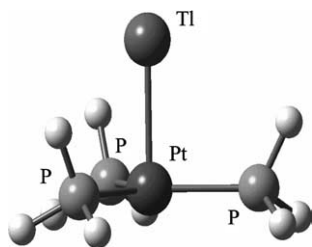


Fig. 1. The intermolecular interaction models of $[\text{Pt}(\text{PH}_3)_3\text{Tl}]^+$.

2. Computational details

A simplified model of the experimental structure with the general formula $[\text{Pt}(\text{PPh}_2\text{Py})_3\text{Tl}]^+$ is depicted in Fig. 1. The structure assumes a C_{3v} point symmetry. In order to avoid the large computational effort, we use phosphine (PH_3) instead of the original diphenyl-2-pyridylphosphine ligands. Hereby, the theoretical model and the experimental information is comparable only for the atoms of Tl and Pt. The calculations were done using GAUSSIAN 98 [11]. For the heavy elements Pt and Tl, we used the Stuttgart pseudopotentials (PP): 18 valence-electron (VE) for Pt and 21-VE for Tl [12]. Two f-type polarization functions were added to Pt ($\alpha_f = 0.70, 0.14$) [13] and Tl ($\alpha_f = 1.0, 0.36$) [14]. Also, the P atom was treated with PP, using double-zeta basis set and adding one d-type polarization function [15]. For hydrogen a valence-double-zeta basis set with p-polarization functions was used [16].

The Pt(0)–Tl(I) intermolecular interaction energy was obtained using each of the following methods: HF, MP2–MP4, CCSD and CCSD(T). Though the computational methodologies do not consider spin–orbit interactions, the complex under investigation is a closed-shell singlet; hereby they should have only a minor importance.

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 [17,18].

3. Results and discussion

Table 1 summarizes the principal geometric parameters obtained for the optimized geometries. The interaction energies and the force constants Pt–Tl obtained in several theoretical levels are shown in Table 2. In this section, we will discuss about the geometries and the energies of interaction Pt···Tl in the complex. The natural bond orbital (NBO) analysis is given in Table 3.

Table 1

Main geometric parameters of the model studied $[\text{Tl}-\text{Pt}(\text{PH}_3)_3]^+$

Parameters	HF ^a	MP2	MP3	MP4	CCSD	CCSD(T)
Pt–Tl (pm)	279.9	266.9	281.3	275.7	279.2	277.3
Pt–P (pm)	242.9	233.6	236.4	235.2	235.7	234.6
P–H (pm)	141.1	141.9	141.5	141.2	141.6	141.6
<P–Pt–Tl (deg)	90.0	90.0	90.0	90.0	90.0	90.0
<P–Pt–P (deg)	120.0	120.0	120.0	120.0	120.0	120.0
<H–P–Pt (deg)	119.2	119.4	120.4	119.7	120.3	119.8

Distances in pm and angles in degrees.

^a Experimental distances and angle in $[\text{Pt}(\text{PPh}_2\text{Py})_3\text{Tl}] \cdot (\text{NO}_3)$ and $[\text{Pt}(\text{PPh}_2\text{Py})_3\text{Tl}] \cdot (\text{CH}_3\text{CO}_2)$ complexes by Pt–Tl = 289.9 and 286.6 pm; Pt–P = 228.6 and 227.6 pm; <P–Pt–Tl = 92.0° and 92.7°, respectively.

Finally, the nature of the intermolecular interactions will be studied as simple inductive and dispersion expressions obtained for the individual properties of the platinum complex and the thallium ion (Table 4).

3.1. Short-distance behaviour

According to Table 1, the main parameters obtained by the method CCSD(T) are alike to the experimental values that those of the HF method. Concerning the Pt–Tl distance and the interaction energy (see Table 2), it is clear that the electronic correlation effects play an important role in the stability of system. The Pt–Tl distances obtained with all methods are close to the experimental ones; however, the distance obtained with the MP2 method is the shortest. It is worth noting that the MP2 approximation overestimates the metallic interactions [17,18]. According to a recent work of Pyykkö and Patzchke [19] about the nature of the Pt–Tl bonds, a distance Pt–Tl between 300 and 280 pm could express a strong closed-shell interaction. The distances obtained in this work indicates that the Pt···Tl contact is a strong closed-shell interaction, which goes beyond the classic metallophilic interaction [20,21]. The Pt–Tl force constants (F) calculated in the complex (also shown in the Table 2) are indicative of a weak interaction.

The magnitude of the energies of interaction obtained varies according to the method used between 134 kJ/mol (HF) and 205 kJ/mol (CCSD(T)). Such magnitude is generally associated with covalent bonds, though the obtained distances are nearest to a weak metallophilic interaction. This might be indicative of an orbital stabilization due to the formation of stable adducts between the fragment of platinum and the thallium ion. The complex is already stabilized at the HF level as can be appreciated in Table 1.

To obtain a better insight on such stabilization, we have depicted in Fig. 2 an interaction diagram for the frontier molecular orbitals of both fragments $[\text{Pt}(\text{PH}_3)_3]$ and Tl^+ . In the figure, the left and right side of the correspond to the frontier levels of the platinum complex and thallium ion, respectively. The centre of the diagram corresponds to the molecular orbitals for the

Table 2
Optimized Pt–Tl distance (R_e), in pm

	HF	MP2	MP3	MP4	CCSD	CCSD(T)
Pt–Tl	279.9	266.9	281.3	275.6	279.2	277.3
ΔE	-134.12 (-0.05087)	-202.63 (-0.07732)	-136.05 (-0.05165)	-205.52 (-0.07840)	-171.57 (-0.06536)	-203.59 (-0.07762)
F	66.1	125.1	66.4	92.7	82.7	97.1

Interaction energies (ΔE), with counterpoise correction, in kJ/mol (in parentheses a.u.). Force constant (F) Pt–Tl, in Nm^{-1} .

Table 3
NBO analysis of the MP2 density for $[\text{Tl-Pt}(\text{PH}_3)_3]^+$, $[\text{Pt}(\text{PH}_3)_3]$ and Tl(I)

System	Atom	Natural	Natural electron configuration
$[\text{Tl-Pt}(\text{PH}_3)_3]^+$	Tl	0.7179	$5d^{10.0} 6s^{1.91} 6p^{0.35} 5f^{0.10} 6d^{0.04} 7p^{0.03}$
	Pt	-0.2984	$5d^{9.23} 6s^{0.73} 6p^{0.11} 7s^{0.01} 5f^{0.11} 6d^{0.10} 7p^{0.01}$
	P	0.1008	$3s^{1.40} 3p^{3.39} 3d^{0.07} 4p^{0.03}$
	H	0.0309	$1s^{0.97}$
$[\text{Pt}(\text{PH}_3)_3]$	Pt	-0.2743	$5d^{9.31} 6s^{0.68} 6p^{0.07} 7s^{0.01} 5f^{0.11} 6d^{0.11} 7p^{0.01}$
	P	0.1158	$3s^{1.41} 3p^{3.35} 4s^{0.01} 3d^{0.08} 4p^{0.04}$
	H	-0.0081	$1s^{1.00} 2p^{0.01}$
Tl(I)	Tl	1.0000	$5d^{10.0} 6s^{2.00} 6p^{0.00}$

Table 4
Finite field calculations (a.u.) of electric properties of $[\text{Pt}(\text{PH}_3)_3]$ and Tl(I) at MP2 level

Properties	$[\text{Pt}(\text{PH}_3)_3]$	Tl(I)
Polarizability (α)	125.7233	18.8141
First ionization potential (IP_1)	0.2710	0.6749

$[\text{Pt}(\text{PH}_3)_3\text{-Tl}]^+$ complex. Two orbitals show a strong interaction: $26a_1$ and $29a_1$, whereas the molecular orbitals remain without changes (except the LUMO level).

Both orbitals generate the bonding ($26a_1$) and antibonding ($29a_1$) sigma levels from dz^2 (Pt) and $6s^2$ (Tl), respectively. These two molecular orbitals are doubly occupied. These results clearly indicated a net effect of no bonding through the orbital interactions.

The natural bond orbital (NBO) [22] population analysis for the complex is shown in Table 3. This analysis is based on the MP2 density. From the Table 3, it is possible to observe a charge transfer from the $[\text{Pt}(\text{PH}_3)_3]$ fragment toward the thallium ion ($0.2821e$) in the

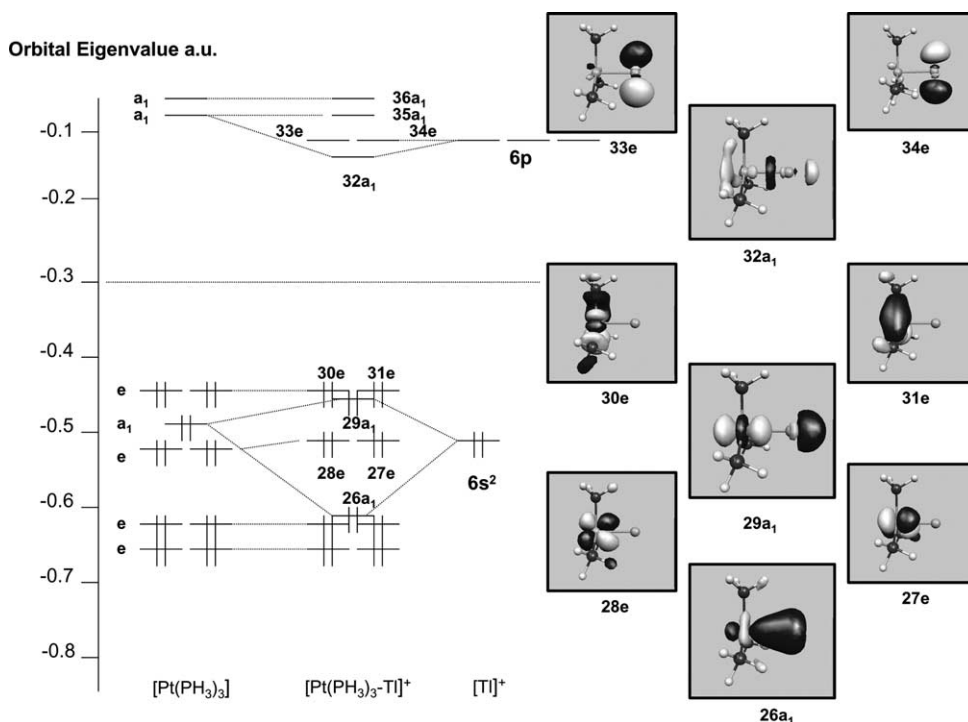


Fig. 2. Interaction diagram obtained for the frontier molecular orbitals for $[\text{Pt}(\text{PH}_3)_3]$ and Tl^+ fragments.

[Pt(PH₃)₃-Tl]⁺ complex. The charge on Tl ion is mainly due to a charge transfer from the hydrogen atoms. The platinum shows no variability in its charge. This would suggest a weak interaction between the platinum complex and Tl ion. The gross population per atom shell shows that for the 6p orbital (0.35e) belonging to thallium take advantage of this charge transfer by increasing its occupation. The charge of the 6s orbital, on the contrary does not change maintaining its inert character. In this system does not exist hybridization between [Pt(PH₃)₃] and Tl orbitals.

3.2. Long-distance behaviour

The HF and MP2 results for the long-distance attraction between [Pt(PH₃)₃] and Tl⁺ are shown in Fig. 3. Energy minima occur at R_e (see Table 2). At the equilibrium distance R_e (Pt–Tl), the differences in energy between HF and MP2 levels corresponds to the electronic correlation effects. At long-range distances, it can be noticed that the HF term is prevailing. We have used the Eq. (1), to describe the terms involved in the limit of large distances. This equation includes the charge-induced dipole (cid) and the dispersion terms, which can be used to understand the predominant mechanism of bonding

$$E = E_{\text{cid}} + E_{\text{disp}} \\ = -\frac{1}{2} \frac{\alpha^{\text{Pt}} q^2}{R^4} - \frac{3}{2} \frac{\alpha^{\text{Pt}} \alpha^{\text{Tl}}}{R^6} \left[\frac{PI^{\text{Pt}} PI^{\text{Tl}}}{PI^{\text{Pt}} + PI^{\text{Tl}}} \right]. \quad (1)$$

Table 4 lists the polarizability (α) and ionization potentials (PI) used for [Pt(PH₃)₃] and Tl(I) obtained at the MP2 level. It is evident from the greater slope observed in the charged-induced dipole interaction curve, that this term predominates over the dispersion force. This may shed light on why Pt–Tl is bonding at

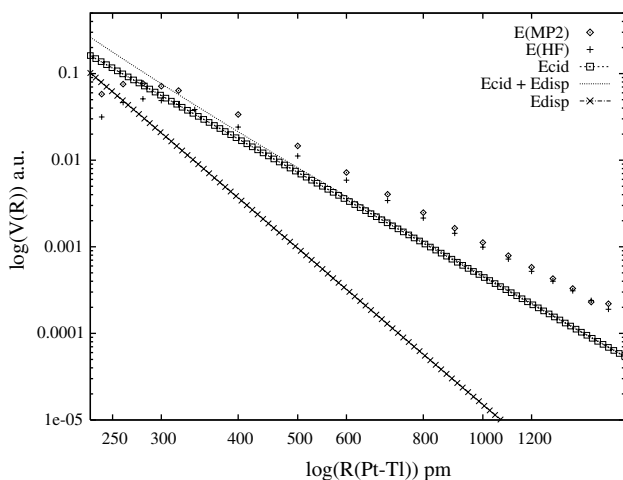


Fig. 3. The calculated interaction energies of the model at the HF and MP2 levels.

the HF level. At the MP2 level, the Pt–Tl equilibrium distance is 266.9 pm, the contribution of the charge-induced dipole term is 68% and the dispersion term is 32%. In this case, the last term is smaller, but not negligible.

4. Conclusions

The calculated binding energies for the [Pt(PH₃)₃-Tl]⁺ complex may be explained by means of dispersion interactions and long-range polarization effects. The leading attractive term in the potential comes from the polarization that [Pt(PH₃)₃] undergoes by Tl⁺. Thus, the largest contribution to the total energy is due to the charge-induced dipole interaction term of Eq. (1), nevertheless the dispersion effects acquire significance near the equilibrium bond lengths. The complex studied here shows an R⁻⁴ behaviour at large distances. Moreover, the charge transfer extracted from the NBO analysis for the [Pt(PH₃)₃] fragment toward the thallium ion, cannot be understood merely as a classic orbital interaction. This is confirmed by frontier orbital analysis, which shows that a formal bond through an orbital interaction does not exist.

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References

- [1] V.J. Catalano, B.L. Bennett, S. Muratidis, B.C. Noll, J. Am. Chem. Soc. 123 (2001) 173.
- [2] V.J. Catalano, B.L. Bennett, H.M. Kar, B.C. Noll, J. Am. Chem. Soc. 121 (1999) 10235.
- [3] V.J. Catalano, B.L. Bennett, B.C. Noll, Chem. Commun. (2000) 1413.
- [4] V.J. Catalano, M.A. Malwitz, J. Am. Chem. Soc. 126 (2004) 6560.
- [5] P. Pyykkö, Chem. Rev. 97 (1997) 597.
- [6] F. Luo, G.C. Mcbane, G.-S. Kim, C.F. Giese, W.R. Gentry, J. Chem. Phys. 98 (1993) 3564.
- [7] R. Wesendrup, P. Schwerdtfeger, Angew. Chem., Int. Ed. 39 (2000) 907.
- [8] R. Wesendrup, J.K. Laerdahl, P. Schwerdtfeger, J. Chem. Phys. 110 (1999) 9457.
- [9] P. Pyykkö, J. Am. Chem. Soc. 117 (1995) 2067.
- [10] J.P. Read, A.D. Buckingham, J. Am. Chem. Soc. 119 (1997) 9010.
- [11] M.J. Frisch et al., GAUSSIAN Inc., Pittsburgh, PA, 1998.
- [12] (a) D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, Theor. Chim. Acta 77 (1990) 12;
(b) T. Leininger, A. Berning, A. Nicklass, H. Stoll, H.J. Wener, H.J. Flad, Chem. Phys. 217 (1997) 19.
- [13] M. Dolg, P. Pyykkö, N. Runeberg, Inorg. Chem. 34 (1996) 7450.

- [14] P. Pyykkö, M. Straka, T. Tamm, *Phys. Chem. Chem. Phys.* 1 (1999) 3441.
- [15] A. Bergner, M. Dolg, W. Küchle, H. Stoll, H. Preuss, *Mol. Phys.* 80 (1993) 1431.
- [16] S. Huzinaga, *J. Chem. Phys.* 42 (1965) 1293.
- [17] P. Pyykkö, F. Mendizabal, *Inorg. Chem.* 37 (1998) 3018.
- [18] F. Mendizabal, G. Zapata-Torres, C. Olea-Azar, *Chem. Phys. Lett.* 382 (2003) 92.
- [19] P. Pyykkö, M. Patzchke, *Faraday Discuss.* 124 (2003) 41.
- [20] P. Pyykkö, *Angew. Chem., Int. Ed.* 43 (2004) 4412.
- [21] P. Pyykkö, F. Mendizabal, *Chem. Eur. J.* 3 (1997) 1458.
- [22] J.E. Carpenter, F. Weinhold, *J. Mol. Struct.* 169 (1988) 41.