

THEORETICAL STUDY OF THE S²-P INTERACTION BETWEEN Tl(I) AND OLEFINIC SYSTEMS ON HYPOTHETICAL [Tl(C₂H₄)₂]⁺ AND [Tl(C₂H₂)_n]⁺ (N = 2,3) COMPLEXES

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ABSTRACT

The attraction between [C₂H₄]₂ and [C₂H₂]_{2,3} and Tl(I) in the hypothetical [Tl(C₂H₄)₂]⁺ and [Tl(C₂H₂)_n]⁺ (n = 2,3) complexes was studied using ab initio methods. It was found that the changes around the equilibrium C-Tl distance and in the interaction energies are sensitive to the electron correlation potential. We evaluated these effects using several levels of theory, including HF, MP2, MP4 and CCSD(T). The equilibrium C-Tl distances in the complexes are in the range of 294 pm to 338 pm. The interaction energy differences obtained at the equilibrium distance range from 55 to 110 kJ/mol at the different levels used. These results indicate that the complexes formed are in the category of van der Waals systems. Also, these results indicated that the interaction between olefinic systems and Tl(I) are a real minimum on the potential energy surfaces.

INTRODUCTION

Closed-shell interactions range from extremely weak van der Waals forces to metallophilic and extremely strong d¹⁰-s² or s²-s² interactions [1-5]. We have reported closed-shell organometallic hypothetical complexes between an olefinic Pi-system (L) and thallium(I) s² [6]. The calculated interaction energies of the [C₂H₂-Tl]⁺ and [C₂H₄-Tl]⁺ complexes were explained in terms of long-range polarization and dispersion interactions, which the attractive term is dominant in the potential coming from the polarization of ethylene and acetylene by Tl⁺. The largest energy contribution is the charge-induced dipole interaction, but dispersion effects are significant near the equilibrium bond length. Moreover, natural bond orbital (NBO) analysis showed a small charge transfer from the olefinic systems to the thallium ion, but this cannot be understood as a classic dative interaction. This was confirmed by an orbital analysis, which shows that no formal bond through an orbital interaction exists. It was also found that the relativistic effect increases the interaction energy by 15% [6]. We extend this work proposing the formation of complexes with two and three olefinic systems.

There are no reported complexes of the [(L)_n-Tl]⁺ type with neutral olefinic Pi-system at the theoretical and experimental levels. Complexes of the Cp-Tl-Cp-Tl⁺ (Cp: pentamethylcyclopentadienyl and pentabenzylcyclopentadienyl anions) type are described in the literature, with ionic interactions prevailing in them [7-10].

In the present work we extend the formation of complexes with two and three olefinic ligands with the formation of the novel [(C₂H₄)₂Tl]⁺ and [(C₂H₂)_nTl]⁺ (n=2, 3) complexes (Figure 1) as model intermolecular interactions (Pi)₂-s² and (Pi)_n-s² in organometallic systems. We estimate the stability of the complexes formed at the HF (Hartree-Fock), MP2 (Møller-Plesset second order), MP4 (Møller-Plesset four order) and CCSD(T) (Coupled Cluster singles, doubles and triples) levels. We report the structure and stability of these compounds and predict the most promising targets for synthetic work.

Computational Details

The models were built so that the Tl(I) interacts with the Pi-system of each ligand. In turn, the ligands may have two possible spatial arrangements: parallel and perpendicular. See Figure 1.

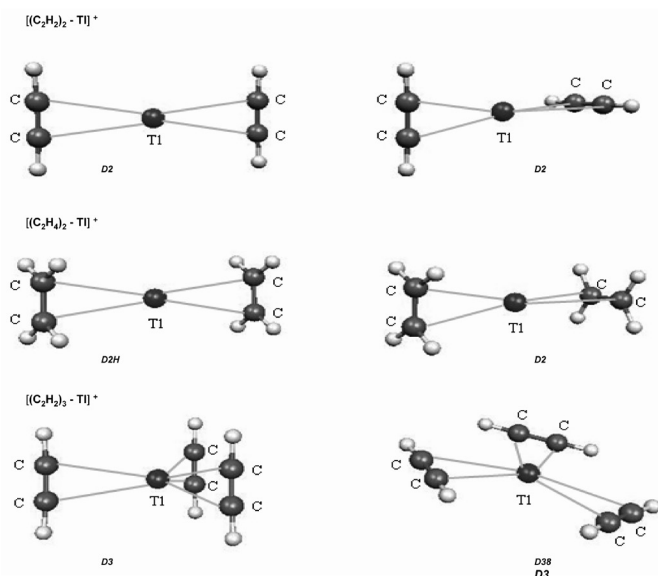


Figure 1. Models of the [(C₂H₂)₂Tl]⁺, [(C₂H₄)₂Tl]⁺ and [(C₂H₂)₃Tl]⁺ complexes.

The calculations were made using Gaussian 03 [11]. For the heavy element Tl we used the Stuttgart quasirelativistic (QR) pseudopotential (PP) 21-VE [12]. Two *f*-type polarization functions were added to Tl ($\alpha_f = 1.0, 0.36$) [13]. Also, the C atom was treated with PP, using double-zeta basis set and adding one *d*-type polarization function [14]. For hydrogen a valence-double-zeta basis set with *p*-polarization functions was used [15].

Fully optimized geometries were determined by the following methods: HF, MP2, MP4 and CCSD(T). Although the computational methods do not consider spin-orbit interactions, the complexes under investigation are closed-shell singles, so they should have only minor importance. The counterpoise correction for the basis-set superposition error (BSSE) was used for the calculated interaction energies [16].

RESULTS AND DISCUSSION

Tables 1-3 summarize the principal geometric parameters and interaction energies C-Tl obtained for the optimized geometries at several theoretical levels. In this section we will discuss the geometries and the interaction

energies of $(C_2H_4)_2 \cdots Tl^+$ and $(C_2H_2)_n \cdots Tl^+$ ($n = 2,3$) in the proposed complexes. Moreover, we have included the study of spatial arrangement in which the ligands are oriented in parallel or perpendicular geometries. As seen in the tables, there is no preferred spatial arrangement.

Table 1. Geometries (pm and deg) and interaction energies ($V(R_e)$, kJ/mol) for $[(C_2H_2)_2Tl]^+$ at the HF, MP2, MP4 and CCSD(T) levels.

	PARALLEL				PERPENDICULAR			
	HF	MP2	MP4	CCSD(T)	HF	MP2	MP4	CCSD(T)
Tl-C	350.8	318.7	325.0	328.1	350.1	318.4	324.6	327.7
C-C	119.2	122.6	130.7	122.5	119.2	122.6	122.7	122.5
C-H	106.6	107.7	107.9	107.9	106.6	107.7	107.9	107.9
CCH°	176.6	176.1	176.1	179.2	176.6	176.2	176.2	176.2
HCCH°	0.2	0.0	0.0	0.0	87.6	88.6	88.9	88.9
$V(R_e)$	-55.0	-76.4	-69.7	-66.5	-55.1	-76.5	-69.8	-66.6

Table 2. Geometries (pm and deg) and interaction energies ($V(R_e)$, kJ/mol) for $[(C_2H_4)_2Tl]^+$ at the HF, MP2, MP4 and CCSD(T) levels.

	PARALLEL				PERPENDICULAR			
	HF	MP2	MP4	CCSD(T)	HF	MP2	MP4	CCSD(T)
Tl-C	358.8	327.3	332.6	335.3	358.9	327.3	332.5	335.5
C-C	132.3	134.4	134.9	134.9	132.3	134.4	134.9	134.9
C-H	108.4	109.3	109.6	109.6	108.4	109.3	109.6	109.6
CCH°	121.6	121.4	121.5	121.5	121.6	121.4	121.4	121.5
HCCH°	-	0.0	0.0	-	90.1	88.9	90.1	90.8
$V(R_e)$	-56.2	-78.1	-69.9	-66.0	-56.2	-78.1	-69.9	-66.1

Table 3. Geometries (pm and deg) and interaction energies ($V(R_e)$, kJ/mol) for $[(C_2H_2)_3Tl]^+$ at the HF, MP2, MP4 and CCSD(T) levels.

	PARALLEL				PERPENDICULAR			
	HF	MP2	MP4	CCSD(T)	HF	MP2	MP4	CCSD(T)
Tl-C	354.6	320.8	327.1	354.6	355.3	320.0	326.6	355.3
C-C	119.2	122.6	122.7	119.1	119.1	122.6	122.7	119.1
C-H	106.6	107.6	107.8	106.6	106.6	107.6	107.9	106.6
CCH°	176.8	176.4	176.2	176.6	176.7	176.2	176.1	176.5
HCCH°	0.0	0.0	1.7	1.8	0.0	0.1	0.0	2.3
$V(R_e)$	-78.6	-109.6	-98.8	-96.0	-78.6	-110.0	-98.7	-96.1

The results of our calculations support the original proposed idea that the $[(C_2H_4)_2Tl]^+$ and $[(C_2H_2)_nTl]^+$ ($n = 2,3$) systems show weak closed-shell van der Waals-type interactions. Concerning the C-Tl distance and the interaction energy, it is clear that electronic correlation effects play an important role in the stability of both systems. The C-Tl distances obtained with all methods are close to the van der Waals distances (from 318 pm to 358 pm). However, the distances obtained at the MP2 level are the shortest. It is worth noting that both approximations overestimate the weak interactions [17,18]. The distances obtained in this work indicates that the C \cdots Tl contact is a weak closed-shell interaction on the $C_2H_4 \cdots Tl^+$ and $C_2H_2 \cdots Tl^+$ complexes. Furthermore, there is no difference between the two possible spatial arrangements of ligands (parallel and perpendicular).

Another manifestation of a weak interaction in the complexes is the dihedral HCCH° angle, which shows a low deviation compared to free ethylene

and acetylene. A different behaviour has been found theoretically [19,20] when the presence of an M^+ cation ($M = Au, Ag, Cu$) on the ethylene ligand causes the rehybridization of the carbon centers from sp^2 to sp^3 , resulting in a partial pyramidalization of the two carbons. The dihedral HCCH° angle shows a strong deviation. This was explained through a synergistic combination of s-donor and p-acceptor interaction between the metal and the olefinic Pi-system, commonly designated as back-donation [21,22].

The magnitude of the interaction energies obtained varies, depending on the method used, between 56 kJ/mol (HF) and 78.1 kJ/mol (MP2) in $[(C_2H_4)_2Tl]^+$, 55 kJ/mol (HF) and 76.4 kJ/mol in $[(C_2H_2)_2Tl]^+$, and 78.6 kJ/mol (HF) and 110 kJ/mol (MP2) in $[(C_2H_2)_3Tl]^+$. Such magnitudes are generally associated with weak interactions. There are no differences between systems with ethylene and acetylene. Only the acetylene complex shows C-Tl distances shorter with respect to the ethylene system. This may be indicative of orbital stabilization due to the formation of stable adducts between the olefinic Pi-system (ethylene and acetylene) and the thallium ion. This is due to the fact that the complexes are already stabilized at the HF level, as can be seen in Tables 1-3. However, we know from the $[(C_2H_4)_2Tl]^+$ and $[(C_2H_2)_2Tl]^+$ complexes that this effect is due to the charge-induced dipole.

To get a better insight of such stabilization, we have depicted in Figures 2 and 3 an interaction diagram of the frontier molecular orbitals of both the olefinic Pi-system (acetylene) and Tl^+ ion fragments at the MP2 level. In the figures, the left and right sides correspond to the frontier levels of the olefinic Pi-system and thallium ion, respectively. The centre of the diagram corresponds to the molecular orbitals of the $[(C_2H_2)_2Tl]^+$ (D_2) and $[(C_2H_4)_2Tl]^+$ (D_3) complexes, respectively. Two orbitals show a strong interaction: 20a and 16a in $[(C_2H_2)_2Tl]^+$ and 25a₁ and 24a₁ in $[(C_2H_4)_2Tl]^+$, while the molecular orbitals remain unchanged (except the LUMO levels). Both groups of orbitals generate the bonding (16a and 24a₁) and antibonding (20a and 25a₁) sigma levels of occupied olefinic Pi (acetylene) and 6s² (Tl), respectively. These two molecular orbitals are doubly occupied. These results clearly indicated a net effect of no bonding through the orbital interactions. A similar diagram is obtained for $[(C_2H_4)_2Tl]^+$, no shown here.

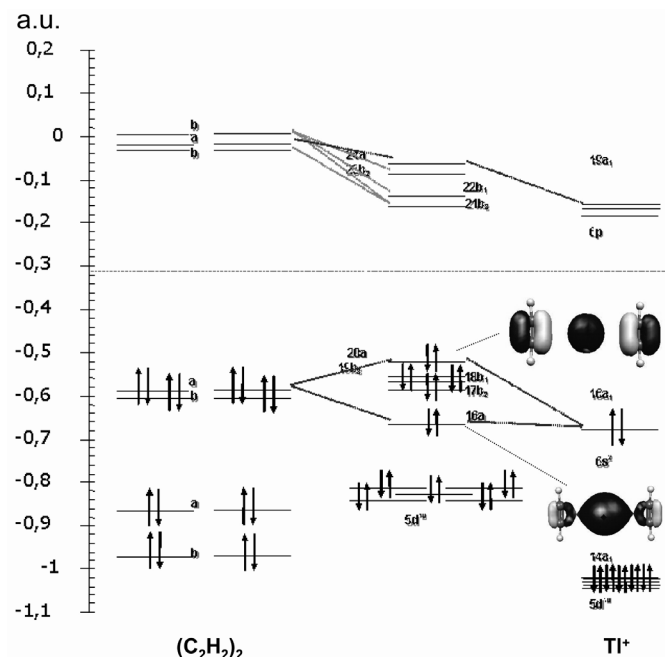


Figure 2. Interaction diagram obtained by the frontier molecular orbitals for the $[(C_2H_2)_2]$ and Tl^+ fragments.

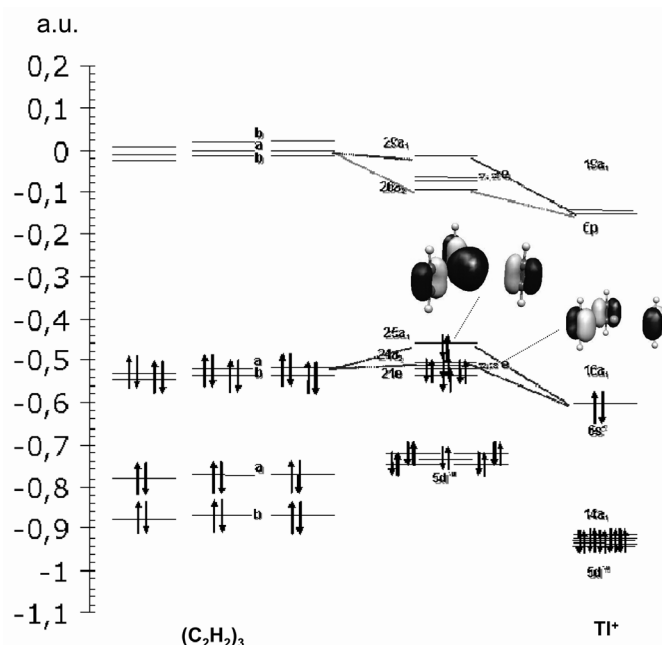


Figure 3. Interaction diagram obtained by the frontier molecular orbitals for the $[(C_2H_2)_3Tl]^+$ and Tl^+ fragments.

The NBO [23] population analysis of the complexes are shown in Table 4. This analysis is based on the MP2 density. In Table 4, it is possible to see a small charge transfer from the olefinic Pi-system (ethylene and acetylene) toward the thallium ion in the complexes under study in both geometries. The charge on the Tl ion is mainly due to a charge transfer from the hydrogen atoms. The carbons show no variability in its charge. This can suggest a weak interaction between the carbons and Tl ion. The gross population per atom shell shows that the 6p orbital (between 0.12e and 0.15e) belonging to thallium takes advantage of this charge transfer by increasing its occupation. This result can suggest a possible orbital interaction between both fragments. The charge of the 6s orbital, on the contrary, does not change, retaining its inert character.

Table 4. NBO analysis of the MP2 density for $[(C_2H_2)_2Tl]^+$, $[(C_2H_4)_2Tl]^+$ and $[(C_2H_2)_3Tl]^+$.

System	Atom	Charge	Electronic Configuration
$[(C_2H_2)_2Tl]^+$			
Parallel	Tl	0.94516	$6s^{1.93} 6p^{0.12} 5f^{0.10} 6d^{0.03} 7p^{0.01}$
	C	-0.23963	$2s^{1.03} 2p^{3.17} 3s^{0.01} 3p^{0.01} 3d^{0.02}$
	H	0.25310	$1s^{0.74}$
Perpendicular	Tl	0.94482	$6s^{1.93} 6p^{0.12} 5f^{0.10} 6d^{0.03} 7p^{0.02}$
	C	-0.23990	$2s^{1.03} 2p^{3.17} 3s^{0.01} 3p^{0.01} 3d^{0.02}$
	H	0.25345	$1s^{0.74}$
$[(C_2H_4)_2Tl]^+$			
Parallel	Tl	0.93782	$6s^{1.93} 6p^{0.12} 5f^{0.10} 6d^{0.03} 7p^{0.02}$
	C	-0.40218	$2s^{1.07} 2p^{3.28} 3s^{0.01} 3p^{0.02} 3d^{0.02}$
	H	0.20877	$1s^{0.78}$
Perpendicular	Tl	0.95259	$6s^{2.00} 6p^{0.05}$
	C	-0.40677	$2s^{1.07} 2p^{3.31} 3p^{0.02} 3d^{0.01}$
	H	0.20931	$1s^{0.79}$

$[(C_2H_2)_3Tl]^+$			
Parallel	Tl	0.90266	$6s^{1.93} 6p^{0.15} 5f^{0.10} 6d^{0.03} 7p^{0.02}$
	C	-0.23443	$2s^{1.03} 2p^{3.17} 3s^{0.01} 3p^{0.01} 3d^{0.02}$
	H	0.25052	$1s^{0.74}$
Perpendicular	Tl	0.89724	$6s^{1.93} 6p^{0.16} 5f^{0.10} 6d^{0.03} 7p^{0.03}$
	C	-0.23289	$2s^{1.03} 2p^{3.17} 3s^{0.01} 3p^{0.01} 3d^{0.02}$
	H	0.24989	$1s^{0.74}$

CONCLUSIONS

The calculated interaction energies of the $[(C_2H_2)_nTl]^+$ and $[(C_2H_4)_nTl]^+$ ($n = 2,3$) complexes could be explained in terms of the interaction energies, where the attractive term is predominant in the potential coming from the polarization of ethylene and acetylene by Tl^+ . The largest energy contribution is the charge-induced dipole, and dispersion effects are significant near the equilibrium bond length. Moreover, the NBO analysis showed a small charge transfer from the olefinic systems to the thallium ion, but this cannot be understood as a classic dative interaction. This is confirmed by an orbital analysis, which shows that a formal bond through an orbital interaction does not exist.

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