

Triphenylstibine complexes of Pt (II), theoretical description and *trans* influence study

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Received 20 July 2001; accepted 21 August 2001

Abstract

Theoretical studies of *cis*-platinum-triphenylstibine complexes have been studied. Two features mainly the distortions and the source of particular *trans* influence were analysed. In the first case the source of the distortion is achieved as a consequence of the steric effect. Meanwhile in the second case, the *trans* influence is indirectly approximated by taking advantage of bond order values obtained from the NBO analysis. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Platinum; NMR; Distortion

1. Introduction

Platinum–triphenylphosphine complexes have been extensively studied [1,2], they are well characterised and many of their chemical features have been well established as for example their *trans* influence [3]. In contrast the corresponding analogues of platinum (II)–triphenylstibine complexes have been less investigated [4].

Earlier investigations by IR and NMR spectroscopy reveal the weaker *trans* influence of stibines than phosphines and arsines [4]. Lately Elding et al. have reported the X-ray structures of Pt–Sb complexes and a similar *trans* influence of Ph₃Sb and Ph₃P was observed, as opposed to what has been reported earlier [12,13]. Very recently our group has published the molecular structures of some platinum–stibine

complexes [5] and by comparing the Pt–Br bond length it has been concluded that the *trans* influence of stibines are comparable to phosphines.

To the best of our knowledge no theoretical study has been undertaken. The absence of crystal structures and theoretical studies on Pt–Sb complexes have given rise to some confusion regarding the *trans* influence of antimony within the group. Therefore, it is worthwhile to carry out a theoretical study on these complexes to study mainly their distortions and *trans* influence.

Following the definition of Venanzi and Pidcock [6,7] as the extent to which some particular ligand weakens the bond *trans* to itself in the equilibrium state of that complexes, we have proposed an indirect way to measure this influence by theoretical calculations. This topic and the source for the particular distortions observed in this compounds are the main aim of this paper.

The molecules under study are shown in Fig. 1, the shapes corresponds both to our geometry optimisation

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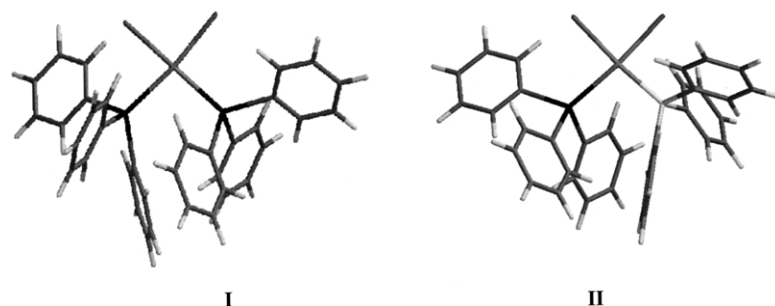


Fig. 1. Molecules under study.

results and to the X-ray study because the theoretical results are in good agreement with the experimental one.

2. Computational details

All calculations were carried out by mean of JAGUAR 3.5 release 42 [8]. The geometry was fully optimised to a local minimum without any symmetry restrictions by using local spin density exchange functional in combination with Vosko, Wilk and Nusair (VWN) correlation functional [9,10] and a LACVP pseudopotential basis set. Larger LACVP* basis set was used for a single point energy calculations. In LACVP and LACVP* basis sets, all elements lighter than potassium were represented by 6-31G and 6-31G* basis sets respectively, while for heavier elements outermost set of core and balance orbitals were represented by double balance contractions adding polarisation functions in the case of LACVP* basis set.

3. Results for *cis*-[PtBr₂(SbPh₃)₂] (I)

This molecule would have a symmetric conformation (belonging to the C_{2v} point group) if we would have the phenyl rings frozen in static and equivalent positions and if there not would be the distortion out of the planar shape. However it presents a little distortion that compels the Pt atom to be out of the plane and the Sb atoms to present a little different bond lengths with respect to the metal centre, this feature is in agreement with the molecular structure determined by the X-ray spectroscopy [5], where Pt atom

is 0.0237 Å above the plane. Therefore, the molecule cannot be classified in any point group.

This distortion is the relevant feature of this molecule, it can be expected the molecule should adopt the more symmetrical shape but the result of the corresponding calculation show a minimisation of energy starting from the planar conformation (calculated at the same level without geometry optimisation) to reach the distorted one. The difference is important (3.67 eV) and enough to change the shape of the molecule; this phenomenon could be analysed as a similar case of a Jahn–Teller distortion [11,12].

The square planar compound contains Pt^{+2} . Then is in a d^8 configuration, this is not a typical case of a good candidate for a Jahn–Teller effect which is present normally in octahedral geometries and other configurations. Furthermore the Jahn–Teller effect commonly is present for a very symmetrical specie which belongs degenerate sets of orbitals, then the degeneration is broken in order to minimise the energy of the orbitals and this is not the case for our study at all. However, the phenomenon here, is very similar in nature because we have a suitable stabilisation caused for the rupture of the C_{2v} symmetry leading to the formation of a distorted planar square. The molecular orbital scheme is very similar in both cases but the energy difference between the eigenvalues corresponding to the HOMO is found to be 0.496 eV favouring the distorted shape.

The source of the distortion may be the presence of the aromatic rings that can develop steric factors. The closest distance between the hydrogen atoms of some rings and the bromine atom is ~ 1.7 Å in the planar geometry, this value is almost the distance of a bond H–Br. Therefore it is expected some kind of repulsion

Table 1
NAOP for molecules I and II

Molecule	Atom	Occupancy
I	Pt	1.9681
I	Sb1	1.3375
I	Sb2	1.3410
II	Pt	1.9971
II	Sb2	1.3460
II	P	1.9999
II	Br1	1.9780
II	Br2	1.9722

that compels the ligands to break the symmetric geometry, the Pt atom to be out of the plane and even the Sb atoms to present a little different bond lengths respect to the metal centre. These features are in agreement with the X-ray analysis [5].

4. Results for *trans*-[PtBr₂(PPh₃)(SbPh₃)] (II)

Again we found a distorted shape molecule, but in this case we have no possibility of a symmetry point group that can allow square planar specie. However, now we have a new feature to consider, the trans influence caused for the two different substituents, i.e. the phosphine and the stibine ligands.

Following Appleton and Bennett [15], the trans influence of a ligand can be approximated using coupling constants for molecules where is present the bond Pt–XR_n ($X = P, As, Sb, \text{etc.}$), and they base their results on the following expression.

$${}^1J_{\text{Pt-P}} \propto \gamma_{\text{Pt}} \gamma_{\text{P}} \alpha_{\text{Pt}}^2 \alpha_{\text{P}}^2 \psi_{\text{Pt}(6s)}(0)^2 \psi_{\text{P}(3s)}(0)^2 (\Delta E)^{-1}$$

Where γ_{Pt} and γ_{P} are the gyromagnetic ratios for the respective nuclei having spin 1/2 and α_{Pt} and α_{P} are the s character of the bonding orbitals used by the respective atoms in the Pt–P bond. These authors claim that the most important factor to consider in this equation is the α_{Pt} term. After they carried out a very interesting study of the trans influence by mean of coupling constants.

In our case we cannot calculate in a simple way coupling constants because the temperature and solvent effects are fundamental to obtain a good result but we can search for the values of α_{Pt} , α_{P} and α_{Sb} in a simple manner i.e. with a natural bond orbital analysis. Thus, we can compare these results with the linear

dependent coupling constant values and make a prediction about the nature of the trans influence.

The values for the electronic occupancy from the Natural Atomic Orbital Population (NAOP) analysis are shown in Table 1 for the two molecules.

Where the Sb1 atom of molecule I was included only to show the difference between both Sb atoms caused by the molecular distortion. Br1 is the one atom placed in position trans to Sb atom, meanwhile Br2 is found in position trans to P atom.

The results show a trend already mentioned by Appleton and Bennett, the coupling constant value for molecule II will be larger than for molecule I which is because of the difference in electronic occupancy on each Pt atom and the dramatic difference between the electronic occupancy between phosphorus and antimony atoms. By considering this a higher trans influence of phosphorus would be expected in comparison to antimony. On the other hand, the calculated Pt–Br bond distances trans to phosphine and stibine are approximately equal as well as the electronic occupation [16], this feature indicates the similar magnitude of trans influence of these ligands phosphine and stibine which was shown earlier experimentally [17]. These result is in agreement with the conclusion of Wendt and Elding [14] but now it has a numerical base to conclude this.

5. Conclusions

Two triphenyl stibine compounds were studied from a theoretical point of view. The compound *cis*-[PtBr₂(SbPh₃)₂] (I) presents a peculiar distortion that has been well characterised by experimental work, this distortion has been analysed from a theoretical sight and it has been found that it arise from a steric factor followed by a pseudo Jahn–Teller effect. On the other hand, the trans influence of *trans*-[PtBr₂(PPh₃)(SbPh₃)] (II) was analysed on the base of a NBO calculation, the result shows the ligands belonging P present bigger trans influence than those with Sb.

Acknowledgements

We thank Ms Teresa Vazques and Ms Sara Jimenez for technical help.

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