Is the metal atom in [M(η^5- Cp)L$_3$] piano-stool complexes tetrahedrically or octahedrically coordinated?

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INTRODUCTION

C_5
rotational symmetry
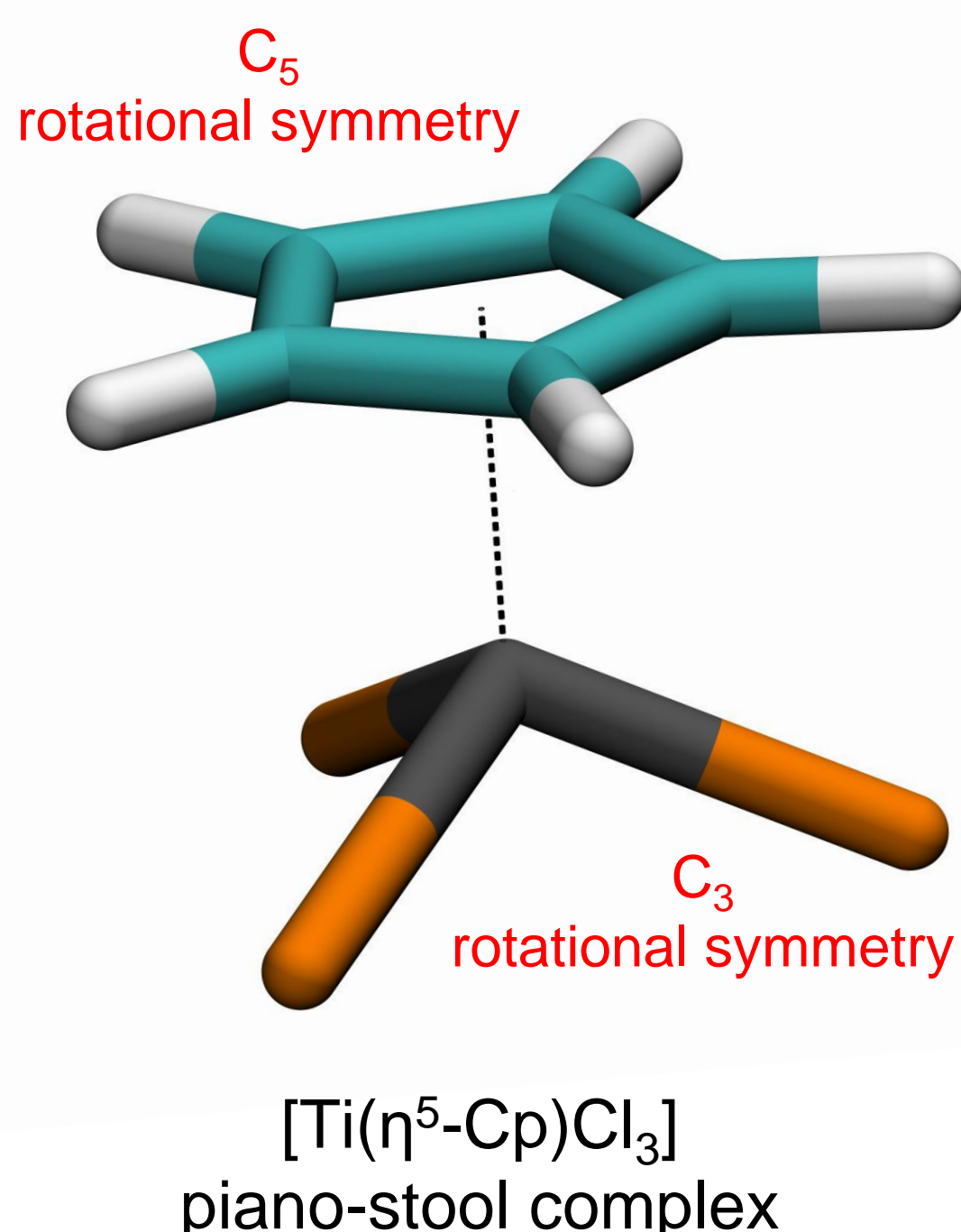
C_3
rotational symmetry

[Ti(η^5-Cp)Cl$_3$]
piano-stool complex

Organometallic complexes with π-bonded ligands such as olefins represent a challenge for the description of the metal coordination sphere in terms of polyhedra. The difficulty arises when one has to decide the set of points to include in the geometrical model. Is it better to represent a π-bonded ethylene ligand by two points associated with the C atoms or just by a single point in middle of the double bond? One particularly difficult case is that of cyclic ligands such as benzene. Do we represent it by just one point at the center of the ring or by the triangle formed by the centers of alternating C-C bonds? A specially interesting case is that of piano-stools,[1] organometallic half-sandwich compounds with one cyclic ligand such as cyclopentadiene and three atomic donor ligands such as Cl, with two incompatible rotational symmetries along a same axis.

Continuous shape and symmetry measures[2], including shape maps[3], plus the pseudo-symmetry analysis of molecular orbitals[4] can be helpful to understand the physical and electronic properties of these compounds and give some clues toward the solution to this kind of problems.[5]

GOALS:

(I) Does the cyclic ligand in piano-stool complexes occupy one single coordination site (tetrahedral shape) or three (octahedral shape)?

(II) Is the shape of the coordination sphere in these molecules related to the electronic configuration of the d orbitals?

METHODOLOGY

Continuous shape measures (CShM)

Continious shape measures are obtained by maximizing the overlap <Q|P> between a problem object Q and a reference object P with respect to all possible shape conserving transformations (translations, rotations and isotropic scaling). From a mathematical point of view, maximizing the overlap is equivalent to a minimization of the distances between vertices, allowing for all possible vertex labelling pairings.

Q   **P$_0$**   **<Q|P>**
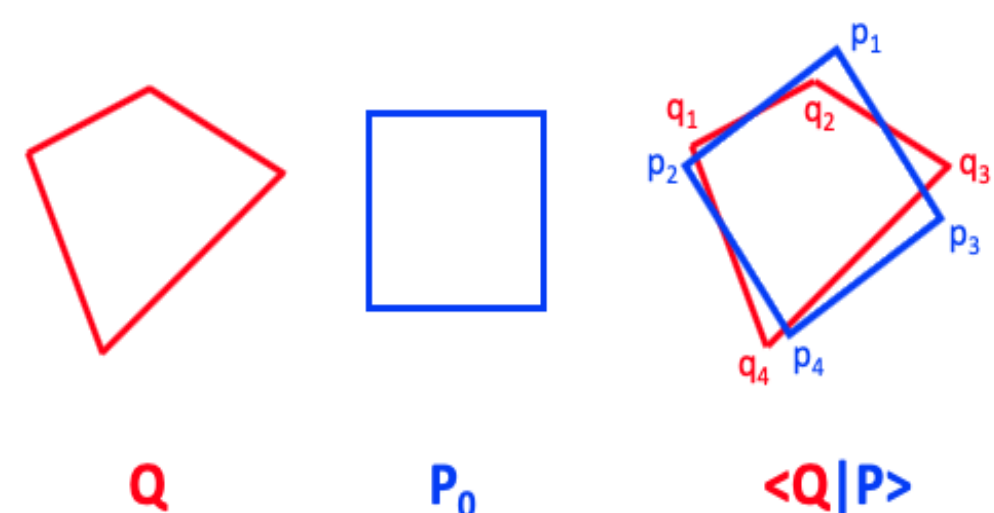
$$S_Q(P) = min \frac{\sum_{k=1}^{N}|\boldsymbol{q}_k - \boldsymbol{p}_k|^2}{\sum_{k=1}^{N}|\boldsymbol{q}_k - \boldsymbol{q}_0|^2} \cdot 100$$

$$0 \leqq S_Q(P) \leqq 100$$

Q and P have the same shape

Q and P are completely different

Pseudo-symmetry analysis for the electronic structure

In a pseudo-symmetry analysys we decompose a function Φ with G symmetry, into components transforming according to the irreducible representations Γ^μ of a given symmetry group G$_0$ (not necessarily coincident with G) with weights given by

$$\omega(\Gamma^\mu) = \frac{d_\mu}{h} \sum_{i=1}^{d_\mu} \sum_{R=1}^{R} D_{ii}^\mu(R) * \alpha_\phi(R)$$
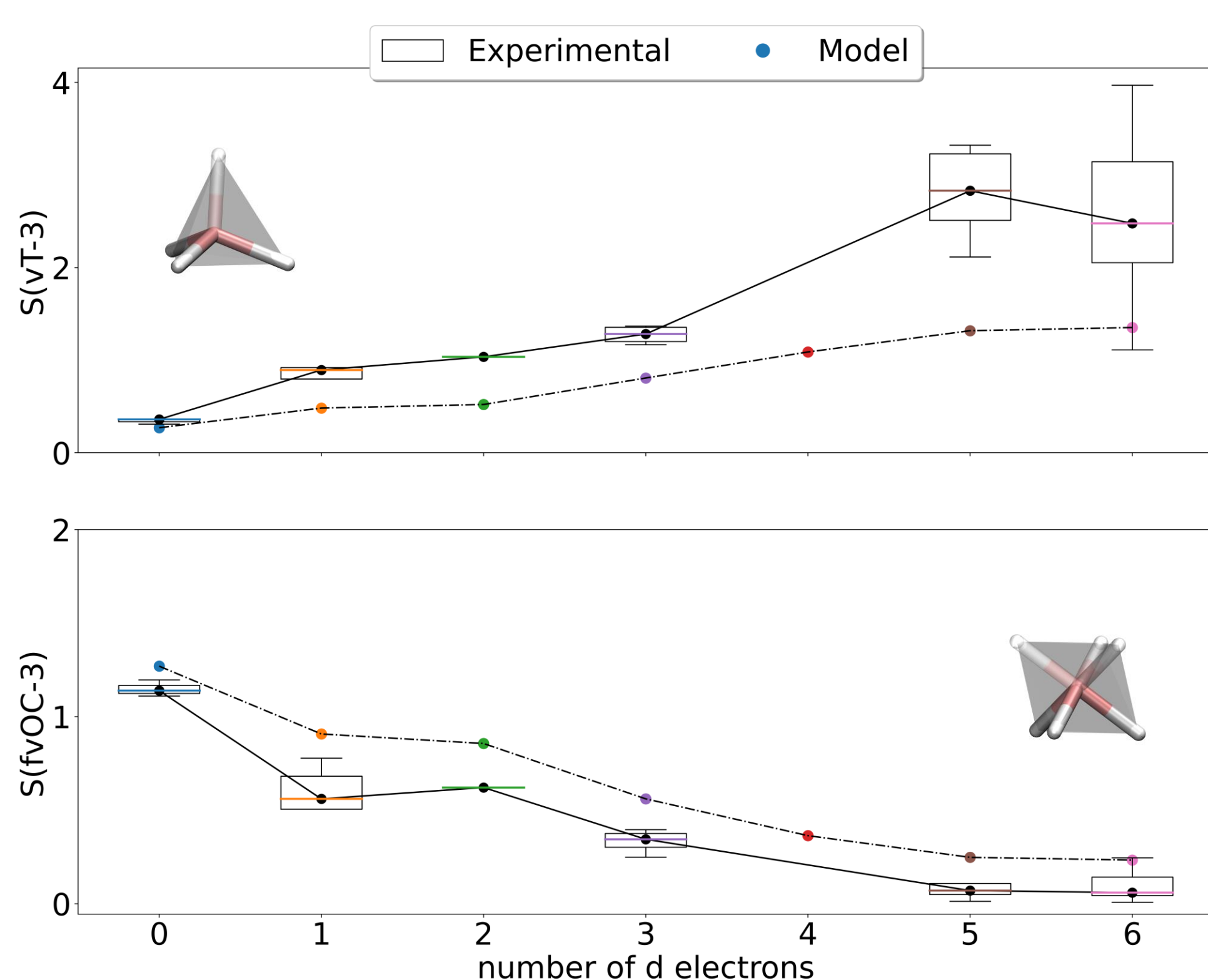
where R are the symmetry operations of G$_0$ and $\alpha_\phi(R)$ their so-called symmetry overlap expectation values (SOEVs):

$$\alpha_\phi(R) = \langle\phi|\hat{O}_R\phi\rangle$$

If G = G$_0$, the $\omega(\Gamma^\mu)$ values are either 1 or 0, indicating if Φ belongs to Γ^μ or not, respectively. When G ≠ G$_0$, then $0 \leqq \omega(\Gamma^\mu) \leqq 1$, indicating the fraction of Γ^μ character of the function.

RESULTS

1 – Shape measures

Experimental (box diagrams) and theoretical (dots) shape measures for the pyramidal ML$_3$ fragments with respect to the vacant tetrahedron (top) and the fac-trivacant octahedron (bottom).

Around 100 experimental piano-stool compound structures retrieved from the Cambridge Structural Data Base (CSD) were analysed. CShMs were calculated for the ML$_3$ fragments with respect to two reference polyhedra: the vacant tetrahedron (vT-3) and the fac-trivacant octahedron (fvOC-3). The trend in the figures shows clearly that an increase in the number of d-electrons implies a shift from a tetrahedral to octahedral shape.

A computational model for piano-stool compounds was set by freezing the cyclopentadiene ring with C$_5$ symmetry and the L$_3$ group of ligands with C$_3$ symmetry along a same axis. Optimization of the molecular geometry at the TPSSh/6-31G(d) (TZVP for the central atom) computational level for this model (dots) reproduces the same trends, except for small shape deviations found for the experimental structures due to distortions that break the perfectly aligned C$_5$ and C$_3$ symmetries fixed in the model.

2 – Molecular orbital energies

Diagram showing the changes in the energies of the d-type OMs with respect to the 100º geometry as a function of the Cp-M-Cl angle. The dashed line corresponds to the total energy for a d^0 occupation.

An extended-Hückel model shows that a d^0 filling leads to a minimum energy for a 118º angle, close that corresponding to a tetrahedral geometry, while filling of the z^2 orbital will tend to minimize the energy for angles closer to the octahedral geometry. The energy of the xy and x^2-y^2 orbitals does not change significatively with the angle, while filling the two more energetic xz and yz, orbitals would lead to smaller angles.

3 – Pseudo-symmetry analysis
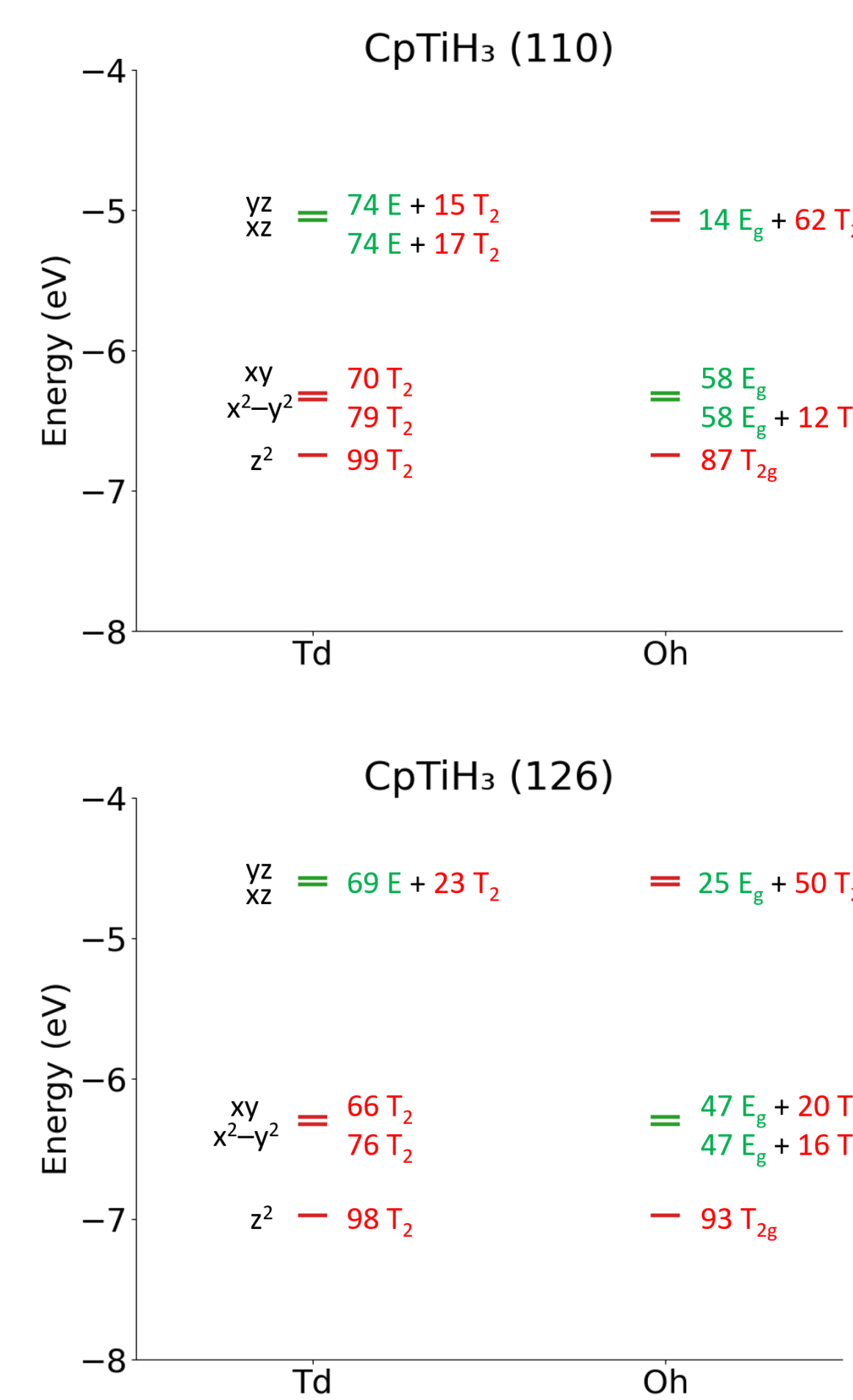
% of E/T$_2$ (left) and Eg/T$_{2g}$ (right) character of the d-type MOs for CpTiH$_3$ with α = 110º (top) and 126º (bottom) geometries

The pseudosymmetry analysis shows that although the splitting pattern of the d-type orbitals is more similar to the 2 over 3 pattern found for complexes with perfect octahedral symmetry, their symmetry behaviour does not match neither the 2E$_g$ over 3T$_{2g}$ pattern for O$_h$ complexes nor the 3T$_2$ over 2E pattern for T$_d$ complexes, irrespective of the geometry of the complex being closer to the tetrahedron or the octahedron.

CONCLUSIONS

- The filling of d-type orbitals dictates the M-Cp-L angle: d^0 ~ 110º (T$_d$) / d^6 ~ 126º (O$_h$)

- A perfect C$_5$/C$_3$ symmetric model for [M(η^5-Cp)L$_3$] reproduces accurately the experimental shape trends

- A molecular orbital energy analysis shows why the filling of d-type MOs controls the molecular shape

- The pseudo-symmetry analysis shows however that changes in the molecular shape are not correlated with changes in the symmetry of the involved orbitals
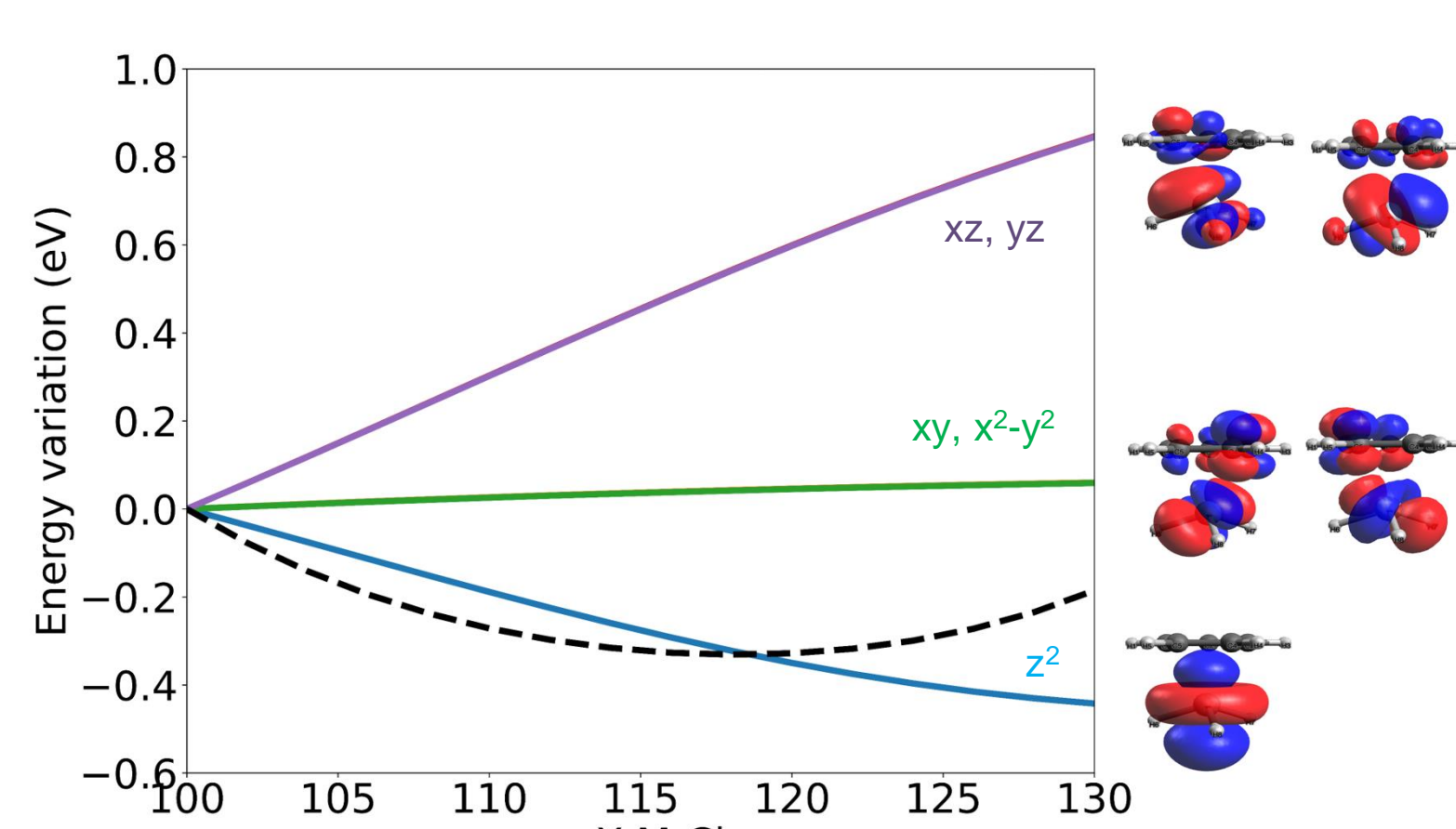
WORK IN PROGRESS

Our current work is aimed towards seeking answers for the following questions:

- Is the effect of d-type orbital filling still present in piano-stools with other aromatic ring ligands?
- How do rings with different rotational symmetries (C$_3$, C$_4$ or C$_6$) affect the pseudo-symmetry of the d-type orbitals?
- How do the d-type orbitals in classical sandwich structures behave compared to those in piano-stools?

REFERENCES

[1] B. Caliskan. Radical Mechanisms in the Metallocenes, Recent Progress in Organometallic Chemistry, IntechOpen (2017)
[2] Zabrodsky, H., Peleg, S. & Avnir, D. Continuous Symmetry Measures. J. Am. Chem. Soc. 114, 7843–7851 (1992).
[3] Cirera, J., Alemany, P. & Alvarez, S. Mapping the Stereochemistry and Symmetry of Tetracoordinate Transition-Metal Complexes. Chem. - A Eur. J. 10, 190–207 (2004)
[4] D. Casanova, P. Alemany, A. Falceto, A. Carreras & Santiago Alvarez. Pseudosymmetry analysis of molecular orbitals. J. Comput. Chem. 34, 1321-1331 (2013)
[5] Alvarez, S. et al. Shape maps and polyhedral interconversion paths in transition metal chemistry. Coord. Chem. Rev. 249, 1693–1708 (2005).