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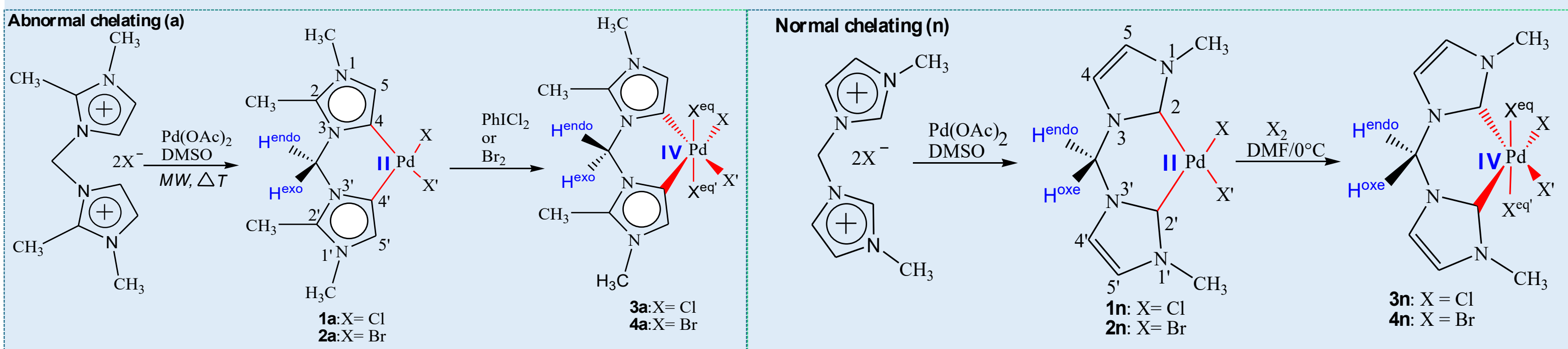
In the past years, the synthesis of natural products and biologically active compounds promoted by transition metal-catalyzed C-H bond activation has raised a growing interest.¹ However, whereas C(sp²)-H activation is facilitated by a higher acidity and more favorable reactant–catalyst interactions, the activation of C(sp³)-H bonds for the formation of C–C or C–X(halogen or heteroatom) bonds is nowadays still a significant and stimulating challenge in the both homogeneous and heterogeneous catalysis.² In this context, the palladium-catalyzed activation of unactivated methyl C-H bonds has been an effective strategy for the construction of carbo- and heterocycles, and has currently attracted much attention.³

The main mode of operation in catalytic reactions has been involved Pd⁰ /PdII cycles. Recently, an alternative PdII/PdIV couple has been aggressively pursued in high oxidation state routes, providing complementary reactivities that are unattainable by Pd⁰ /PdII couples. Several research groups have developed some complexes related to these all Pd oxidation states using either chiral phosphine or N-heterocyclic carbene (NHC) as ligands. Due to their catalytic reactivity in C-H activation processes, this field is showing an increasingly larger scope of applications in various areas of organic synthesis.

However, they mostly rely on the use of homogeneous catalytic systems, which, although very efficient, are usually very difficult to recover and recycle. To overcome this issue, bis-N-heterocyclic carbene ligands (NHCs)⁴ appeared to be a suitable choice as ancillary support for Pd^{II} and Pd^{IV} due to their known propensity to stabilize highly oxidized metal centers without ligand dissociation. According to their catalytic reactivity in C-H bond activation/functionalisation/cyclisation catalysis, it is the time to promote bis-N-heterocyclic carbenes from the status of emerging total alternative to ubiquitous phosphines to the higher status of well established ligands in catalysis. Such is our main motivation for this project.

Aim:

To explore the novel Pd^{II} and Pd^{IV}- CH₂-bridged Bis-N-Heterocyclic Carbene Complexes and their effect on C-H activation/cyclization promoted by a homogeneous catalysis: using quantum chemistry investigation.



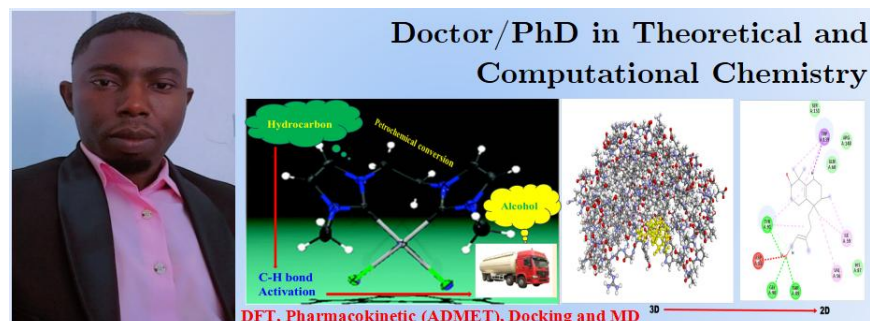
Scheme 1. Pd^{II} and Pd^{IV}- CH₂-bridged Bis-N-Heterocyclic Carbene complexes C-H bond activation

Objectives:

- ❖ Track the nature of the chemical bond and thier electronic bond properties wihtin Pd^{II} and Pd^{IV}- CH₂-bridged Bis-N-Heterocyclic Carbene Complexes;
- ❖ Deciphering the direct C-H bond activation and cyclization mechanism reactions of organic substrates catalyzed by novel PdII and PdIV- CH₂-bridged Bis-N-Heterocyclic Carbene Complex.

5. Reference

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- 2.J. C. K. Chu, T. Rovis, Angew. Chem. Int. Ed. 2018, 57, 62–101; Angew. Chem. 2018, 130, 64–105;
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Jean Moto Ongagna
PhD in computational and Theoretical chemistry
Department of Chemistry



2. Results Obtained

2.1. Geometrical considerations of complexes

- La–Pd and Pd–X bonds lengths close to the experimental data from previous Strassner and Scott McCall studies on the same systems.

- The complexes adopted a slightly distorted square-planar and tetrahedral in Pd^{II} and Pd^{IV} environments, respectively.

- The structure is indicative of a flexible boat-like conformation and pseudo-C_{2v} symmetry. (See Fig. 1). (See, Fig. 1)

2.2. Reactivity and Stability of complexes

Reactivity indices: conceptual DFT (CDFT)

First consideration: Based on the electrophilicity scale, which classifies chemical compounds into strong ($\omega > 1.5$ eV) and moderate ($\omega > 0.8$ eV)⁵ electrophiles, after calculating the electrophilicity it was shown that:

- All the complexes studied are strongly electrophilic.
- Pd^{IV} complexes serve as preferential electrophiles in the C-H bond activation reactions: **3a > 3n > 4a > 4n**.

Second consideration: Based on MESP

- Confirmation of the electrophilic character on all complexes: preferential site on chloride atoms (see, Fig. 2).

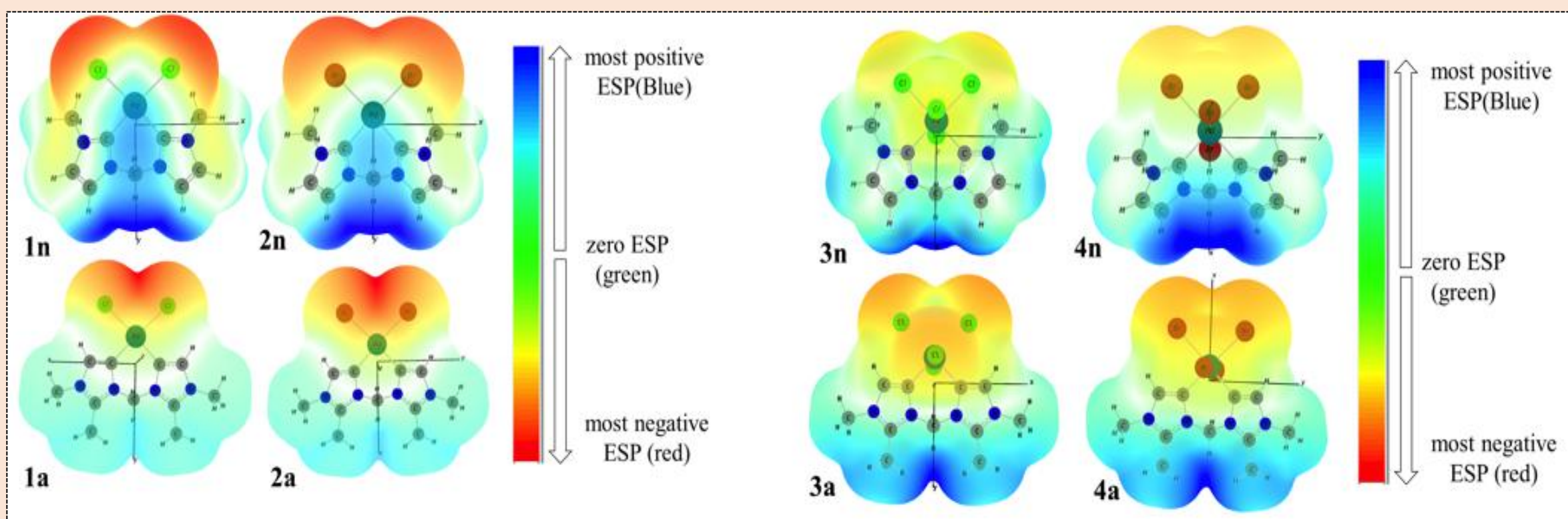


Figure 2. 3D MESP of Pd^{II} and Pd^{IV} complexes mapped onto electron density isosurfaces of value 0.02 a.u.

Stability: Thermodynamic considation

According to the binding energy (E_{bind}), chloride complexes give better stability in all Pd^{II} and Pd^{IV} complexes. (see, Table 1).

Stability: frontier molecular Orbitale consideration

The lower kinetic stability of bromide PdII and chloride PdIV complexes is highlighted by the $E_{\text{LUMO-HOMO}}$ energy gap : $\Rightarrow$ greater reactivity. (see, Fig. 3)

This point of view could justified the choice for LaPd^{II}Br₂ or LnPd^{II}Br₂ and LaPd^{IV}Cl₄ or LnPd^{IV}Cl₄ complexes as catalysts for the direct C(sp²)-H and C(sp³)-H bonds activation/functionalization and/or cyclization reactions.^{10, 11, 21.}

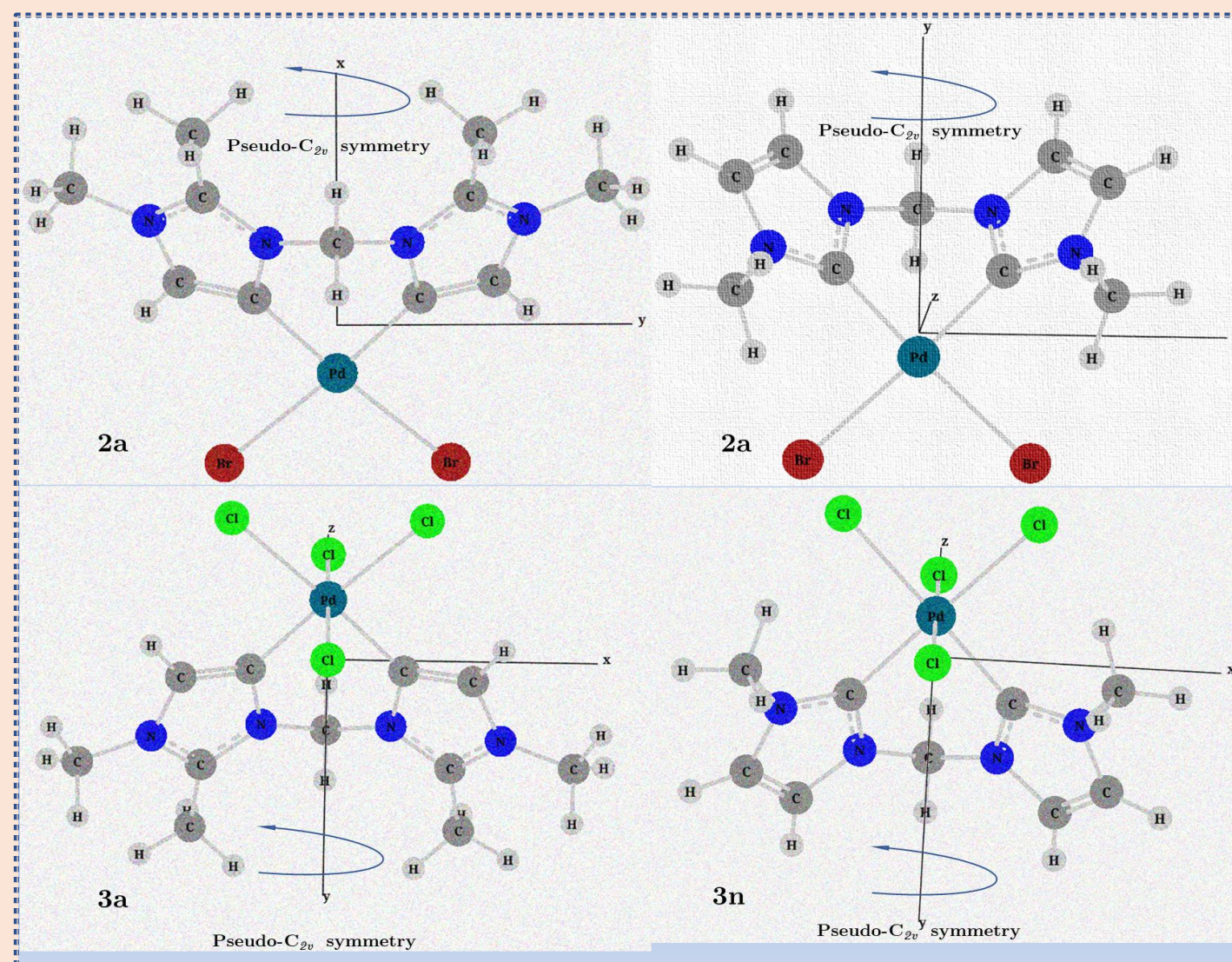
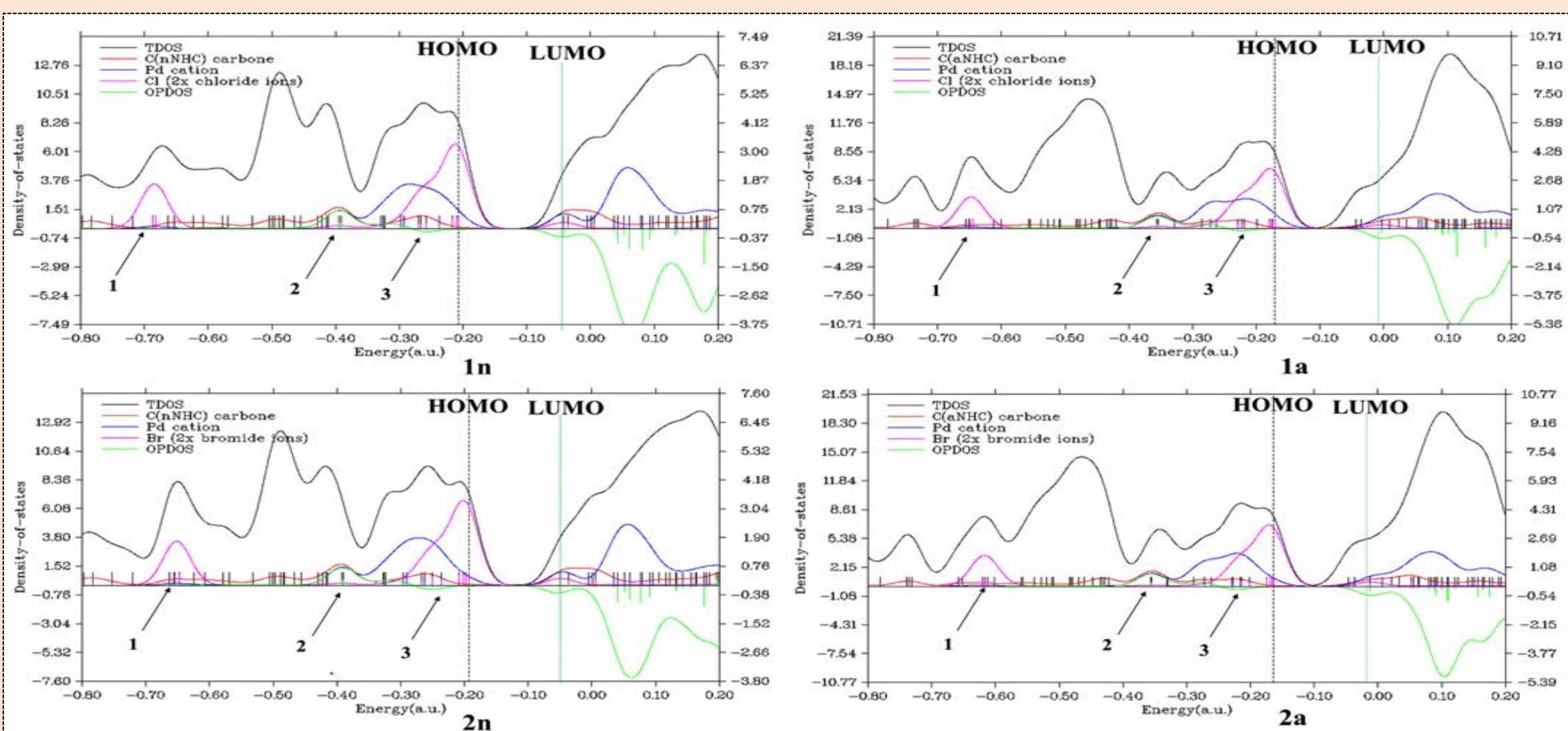


Figure 1. geometrical representation of some optimized complexes

Table 1. Electronic chemical potential (μ), chemical hardness (η), global electrophilicity (ω), Gibbs free enthalpy (ΔG), and binding (ΔE_{bind}) energy of complexes.

Complex	μ (eV)	η (eV)	ω (eV)	ΔG^0 (kcal/mol)	E_{bind} (kcal/mol)
1n	-3.40	2.24	2.59	-45.2	-58.36
2n	-3.30	1.95	5.59	-2265.3	-2280.41
1a	-2.94	1.74	2.48	-44.6	-57.10
2a	-2.86	1.60	2.56	-33.9	-45.81
3n	-3.69	0.51	13.37	-102.3	-117.97
4n	-3.96	0.78	10.11	-4544.5	-4563.95
3a	-3.77	0.46	15.51	-111.7	-126.13
4a	-4.04	0.72	11.29	-92.2	-107.31

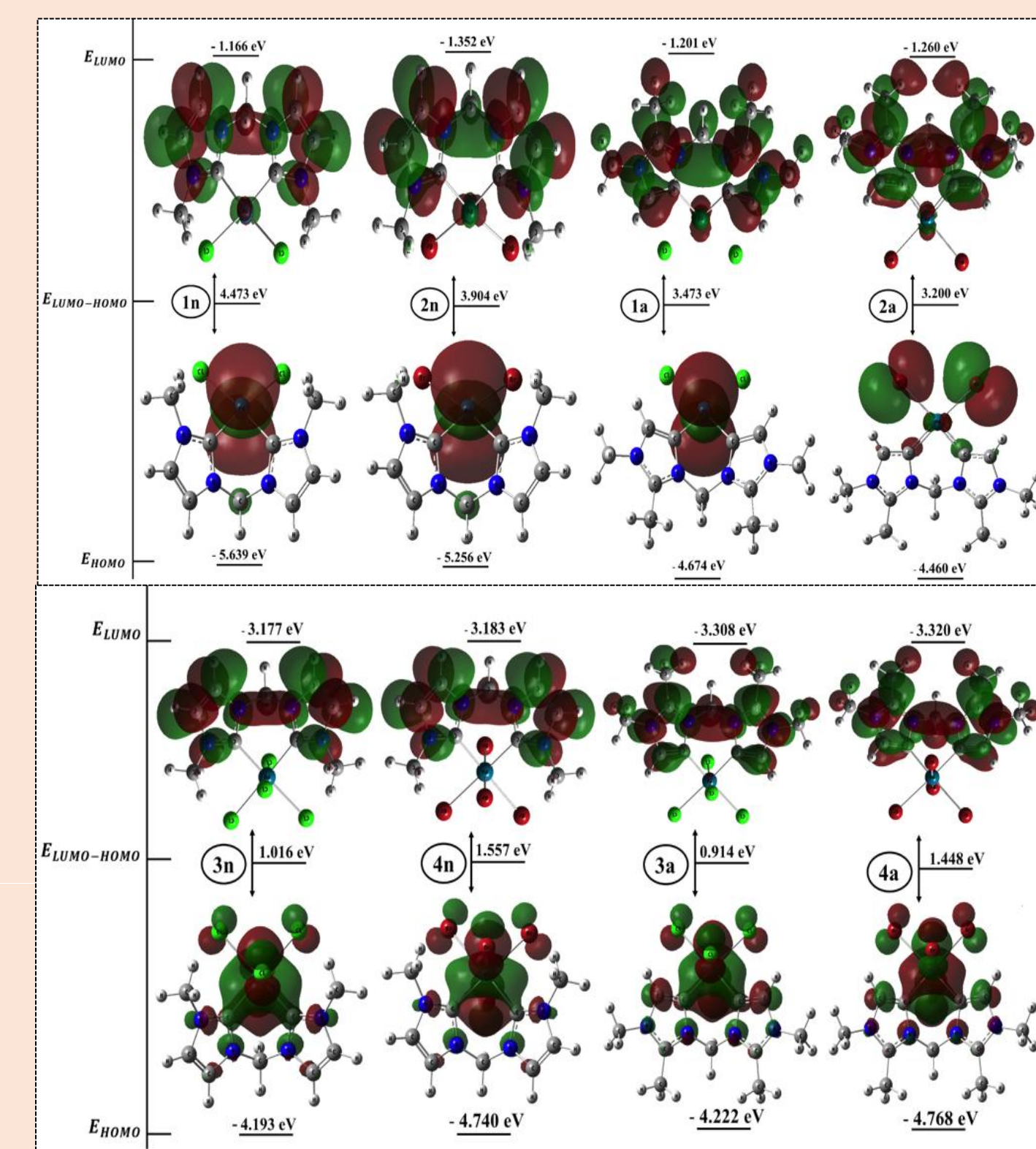


Figure 3. Molecular orbital surfaces plot and energy related for the HOMO and LUMO of all complexes in ground states, isosurfaces value 0.02 a.u.

Figure 4. DOS, PDOS and OPDOS map of 1n, 2n, 1a, and 2a complexes.

2.1. La-Pd, Ln-Pd and Pd-X Bonding properties within complexes

□ NBO consideration

La-Pd, Ln-Pd and Pd-X bonds are mainly composed of s-type, p-type and d-type orbitals corresponding to σ -bonding orbitals and sdp² hybridization

The “d” character of Pd in these both hybridizations increase when going from Pd^{II} to Pd^{IV} complexes and decrease when passing from abnormal to normal complexes.

La-Pd and Ln-Pd σ -bonding are greater polarised towards the C_{nNHC} and C_{nNHC} carbenic atoms

average contributions: 23.13 - 32.08% for Pd and 69.55 - 76.87% for carbenic carbon atom resulted.

□ Topological considation

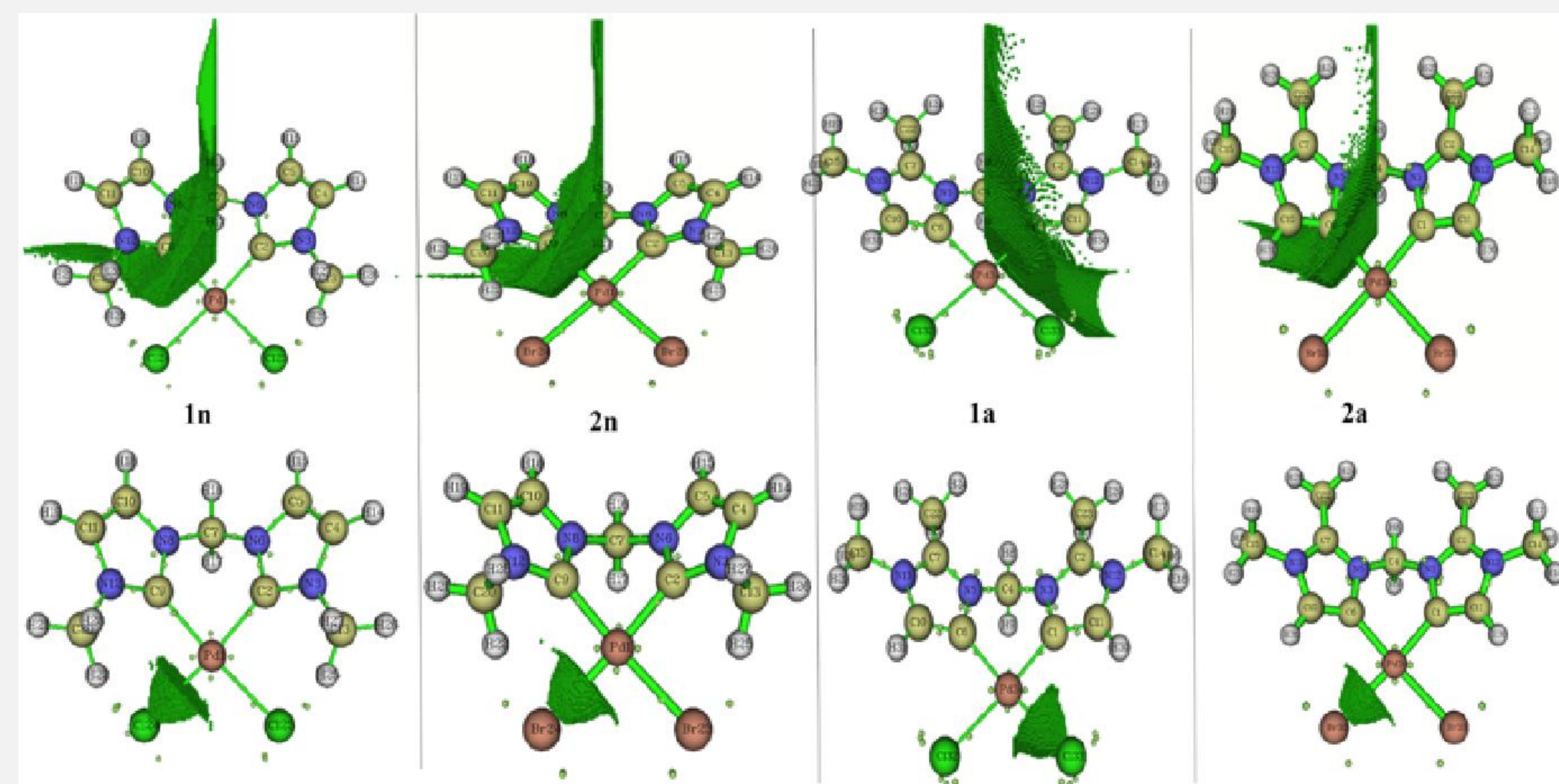


Figure 5. Population density of ELF basins between C-Pd and Pd-X bonds

3. Conclusion

The calculated results show that the nature of the ligand and the coordinating halide ion determine the strength of the C-Pd and Pd-X bonds, depending on the oxidation state of the palladium. These two bonds can be fine-tuned to achieve better catalytic activity by the use of appropriate organic reactant. In fact, this can be achieved by making the Pd carbene bond much stronger through σ -donation and π -back-donation and also by making the Pd-X bond weaker by choosing a suitable halide (X).

4. Result prospects

To explore the novel Pd^{II} and Pd^{IV}- CH₂-bridged Bis-N-Heterocyclic Carbene Complexes and their effect on C-H activation/cyclization promoted by a homogeneous catalysis: using quantum chemistry investigation

