

Abstract

The research of catalytic systems able to activate and functionalize the C-H bonds at low cost have stimulated a particular interest from both a scientific and economic viewpoint. The conversion of methane into methanol catalyzed by Pd-bis(NHC) complexes is one of the advances in organometallic catalysis [1-3]. This reaction highlighted the reactive power of theses complexes. Although a great deal of work has been carried out on these complexes, some factors governing their reactivity have not yet been elucidated. This research work is devoted to examine the influence of alkylene bridged and chelating mode on the topological, electronic and bonding properties of a series bis-(NHC)-palladium complexes. The optimized geometries of these complexes were performed using generic basis set (Lanl2DZ for halogen and palladium atoms and 6-31G(d)) in gas phase and DMSO. DFT approaches combine to QTAIM, NBO, CDA, EDA, and DFT-conceptual analysis were used to analyse Pd-C and Pd-X bonding interaction within bis-(NHC)-palladium complexes. Our data indicated that higher activation of Pd-C bonds has been found out for phenyl and nitro complexes. Most stable Pd...C interactions have been detected for abnormal mode with methylene bridge. The energy decomposition analysis (EDA) indicates that the better electrostatic character is obtained by hydrogen and phenyl complexes in both chelation modes. In both chelation modes, the hybridization around the metal cation for the Pd-C bond has been found to be almost sp²d for methylene-bridged palladium complexes (in both media). But, this hybridization becomes sp³ contrary for ethylene bridge complexes. By the means of the energy decomposition analysis, Pd...C interactions have shown to be stronger for ethylene bridged abnormal complexes (in gas phase). By contrast, their Pd...X interactions are weaker. The donation/back-donation ratio (d/b) values of [bis(NHC)]...[PdX₂] interactions demonstrated that these are Fischer carbene. The ethylene bridged abnormal complexes have therefore been elected as palladium complexes with better catalytic activities.

Keywords: Bis-(NHC)-palladium complexes, QTAIM, Charge and Energy Decomposition Analysis, Alkylene bridged.

I-INTRODUCTION

1-Background of the state of art

The effects of climate change linked to the release of anthropogenic greenhouse gases are increasingly perceptible in our environment. Indeed, if nothing is done to limit their production, our planet is heading for a huge catastrophe. The 2007 forecasts by the intergovernmental panel on climate change show that global warming is unequivocal, with a temperature range of 1.1 to 6.4°C by 2100 [1]. It should be noted that a temperature rise of +2°C would lead to the loss of 30% of animal biodiversity, desertification in the tropics and would exacerbate the problems of access to drinking water from which some countries are already suffering. In view of the imminence of the subject, at the political-diplomatic level, party conferences (COP) are organized regularly with a view to finding policies to reduce the production of GES. However, the measures taken at these summits have been slow to be implemented because of the refusal of some major powers to respect their commitments. From a scientific point of view, the direct oxidation of natural gases, of which there are abundant reserves worldwide and which mainly consist of methane, into methanol or diesel, represents a new environmental and economic challenge. After the failures linked to the use of synthesis gas in the conversion of certain GHGs (CO₂, methane, etc.) into liquid derivatives at very high temperatures (800°C) [2]. The cumulative work of Strassner et al [3-5] on the petrochemical conversion of methane at low temperature (180°C) into alcohol catalyzed by metal-bis-(N-heterocyclic carbene) complexes remains limited today to laboratory scale. Cheong et al have shown that complexes can also be used as catalysts in the recovery of chemical wastes such as CO₂, CO, and inorganic carbonates (K₂CO₃, KHCO₃, Na₂CO₃ and NaHCO₃) reducing the carbon balance [6].

2- Problematic

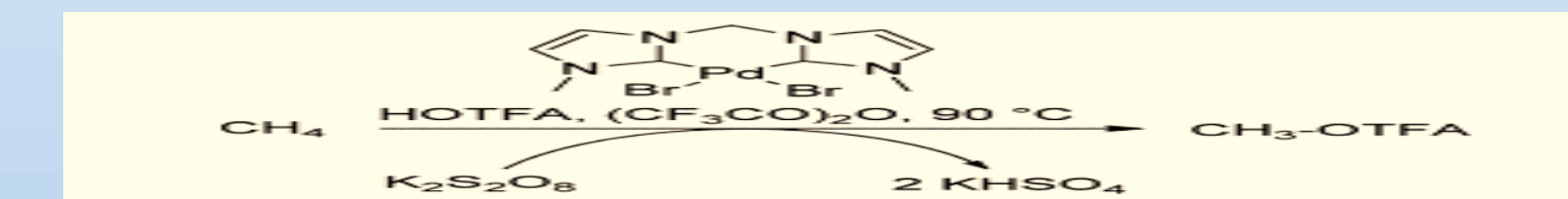
Given the importance of these discoveries, the lack of knowledge of the electronic structure linked to the catalytic activity of these Metal-bis(NHC) complexes makes their use on an industrial scale difficult. This is at the root of the controversy that has led us to question the factors really responsible for the high reactivity of these complexes in catalysis.

3- General objective

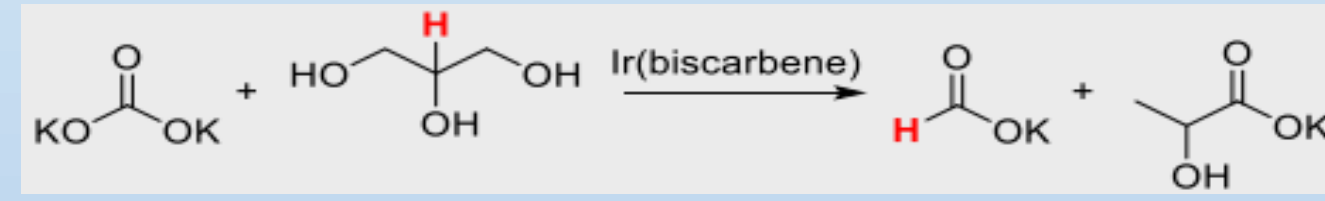
Optimize the Munz et al reaction on the oxidation of lightweight alkanes to alcohols

4- Specific objectives

- To model and study the structural properties of a series of 24 palladium-bis-(N-heterocyclic carbene) complexes in order to identify the one with the best catalytic activity.
- Simulate the reactivity of this complex with alkanes.



Scheme 1: Direct Catalytic Methane Oxidation by Chelated Pd Bis(NHC) Complexes (Munz reaction)



Scheme 2: Transfer Hydrogenation of K₂CO₃ in Glycerol (Cheong reaction)

III-CONCLUSION

Despite the many studies carried out on N-heterocyclic carbene since 1991 and the discoveries made to date, they continue to impress the scientific community. Their ability to chelate the majority of transition metals, their high reactivity and the multiple configurations adopted by the complexes formed mean that they can be used in fields other than catalysis, fine chemistry and medicine, creating a new paradigm for research.

IV-REFERENCES

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II-RESULTS

1- Geometrical details

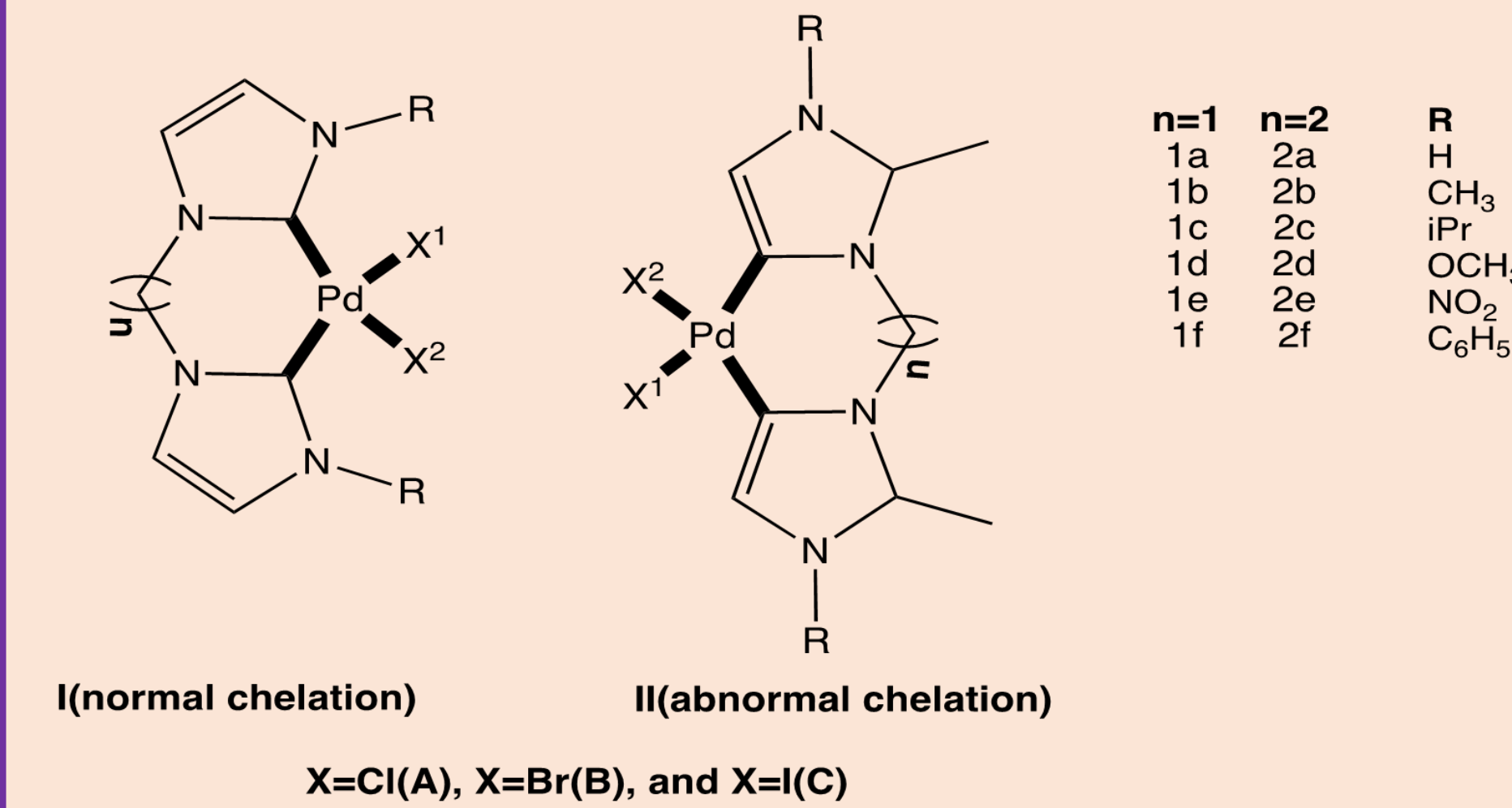


Figure 1: Chelating mode and numbering system of bis(NHC)PdX₂ complexes under investigation

2-Stability and bonding property

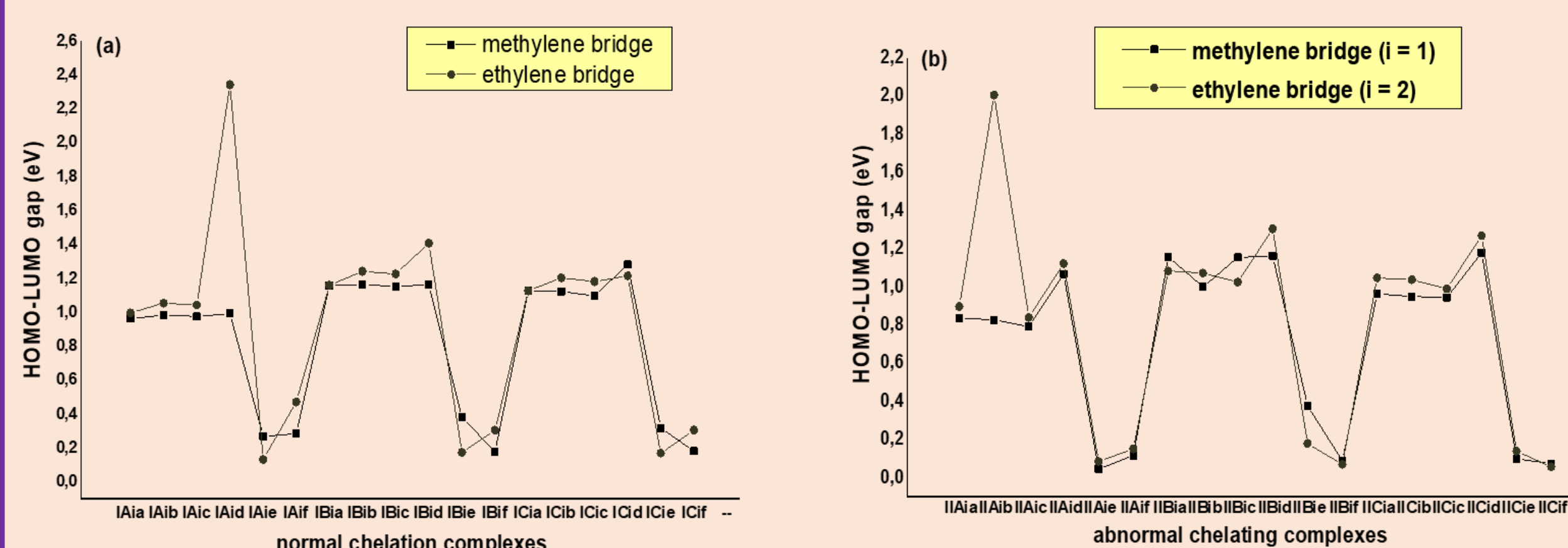


Figure 2: Graphical drawing of the influence of bridge type on the stability using HOMO-LUMO gap as descriptor (normal (a) and abnormal (b) chelating mode)

3-Charge decomposition analysis

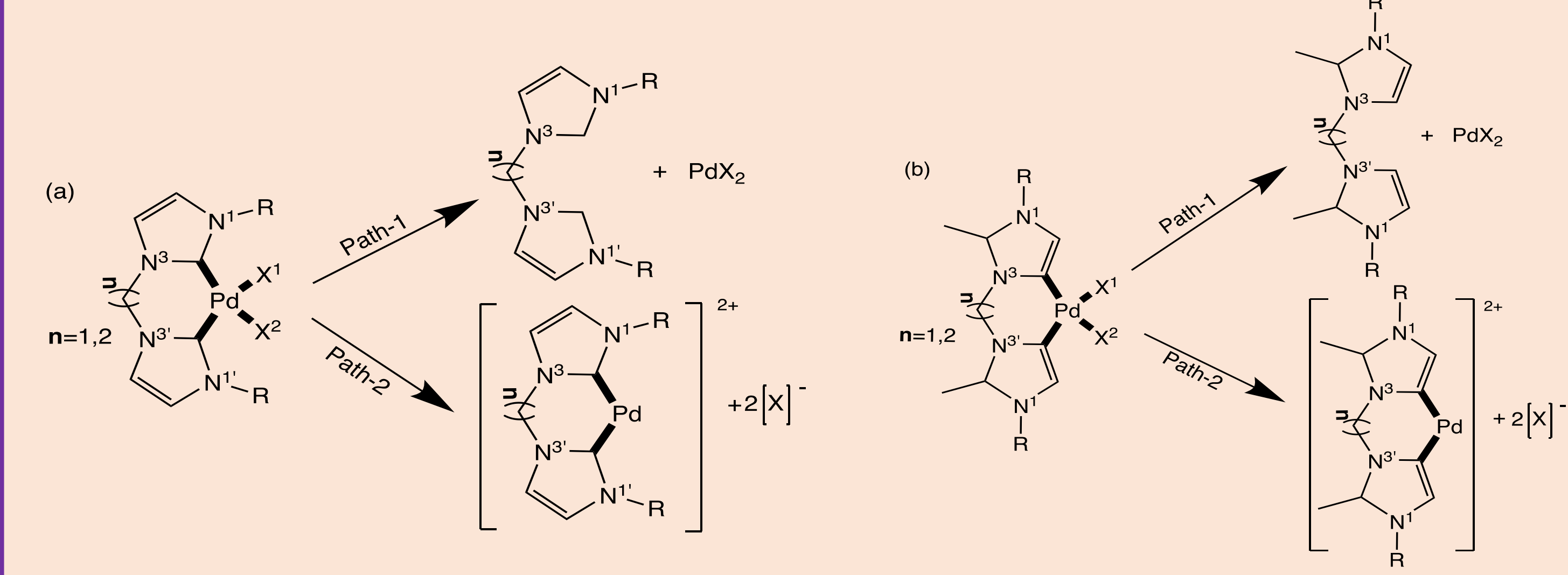


Figure 4: Different paths (a and b) of the decomposition for normal (a) and abnormal (b) complexes along the EDA and CDA analysis.

Table 1: Relevant geometrical parameters of optimized methylene bridged normal complexes (n=1) at B3PW91/Gen level in gas phase

	X=Cl						X=Br						X=I					
	IA1a	IA1b	IA1c	IA1d	IA1e	IA1f	IB1a	IB1b	IB1c	IB1d	IB1e	IB1f	IC1a	IC1b	IC1c	IC1d	IC1e	IC1f
Bond length																		
Pd-C ₂	1.968	1.994 1.966 ^[7]	1.993	1.990	1.976	2.005	1.984	2.003 1.983 ^[8]	2.003	2.00	1.98	2.003	2.003	2.014 1.989 ^[9]	2.017	2.022	2.004	2.018
Pd-C ₂	1.968	1.994 1.975 ^[7]	1.993	1.990	1.976	1.983	1.984	2.003 1.971 ^[8]	2.003	2.00	1.98	2.003	2.003	2.014 1.988 ^[9]	2.017	2.022	2.004	2.018
Pd-X ₁	2.431	2.412 2.365 ^[7]	2.413	2.404	2.396	2.417	2.561	2.549 2.500 ^[8]	2.551	2.54	2.53	2.538	2.715	2.706 2.657 ^[9]	2.710	2.692	2.693	2.698
Pd-X ₂	2.431	2.412 2.365 ^[7]	2.413	2.404	2.396	2.398	2.561	2.549 2.494 ^[8]	2.551	2.54	2.53	2.538	2.715	2.706 2.647 ^[9]	2.710	2.692	2.693	2.698
Bond angle																		
X ₁ -Pd-X ₂	96.9	93.1 90.33 ^[7]	93.4	92.5	95.8	93.3	94.5	92.8 92.6 ^[8]	93.2	92.2	94.7	94.0	92.9	93.3	92.8	92.0	94.1	93.6
C ₂ -Pd-C ₂	87.6	86.2 83.78 ^[7]	86.2	85.1	86.6	85.3	87.5	85.7 83.2 ^[8]	85.6	84.8	86.2	86.7	87.2	85.2 83.2 ^[9]	85.1	86.2	85.8	86.2

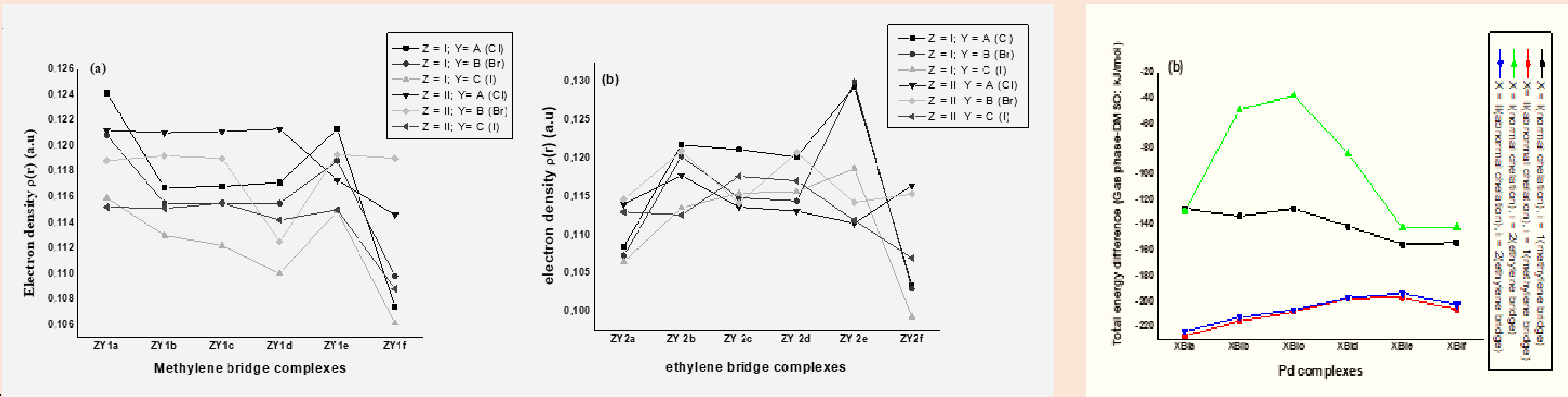


Figure 3: Pd-C graphical drawing of the influence of chelating mode of methylene (d) and ethylene (e) bridged complexes on electron density.

Figure 4: Energy total difference (gas phase-DMSO) of Pd-bis(NHC) complexes

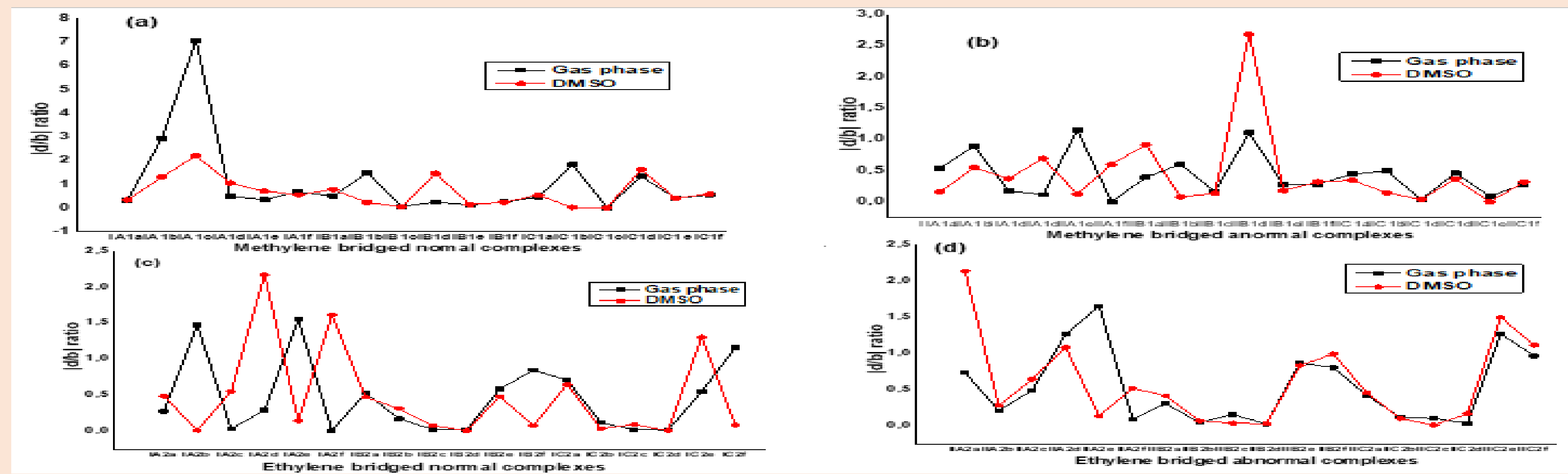


Figure 5: Graphical drawing of evaluation of donated/back donated ratio in methylene (normal (a) and abnormal (b)) and ethylene (normal (c) and abnormal (d)) bridged complexes for [Bis (NHC)]...[PdX₂] interaction within.