J. Environ. Econ. Chem. Process.,: Vol. 2, No. 3, (2025) 96–99

Journal of Enviromental Economics & Chemical Processes (JEECP)

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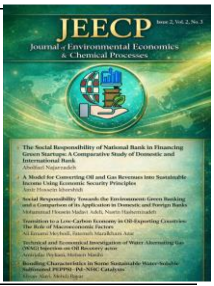
journal homepage: *WWW.JEECPJournal.com*



Bonding Characteristics in Some Sustainable Water-Soluble Sulfonated PEPPSI–Pd–NHC Catalysts

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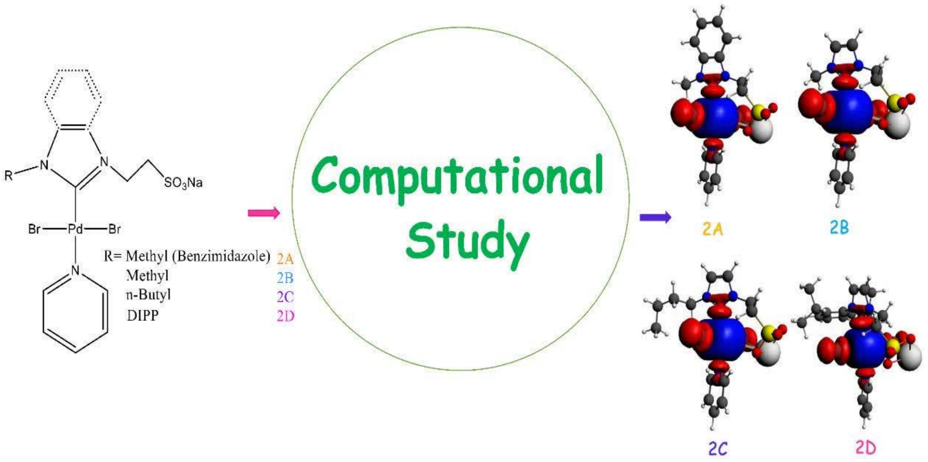
PAPER INFO

Paper history:
Received 4/14/2025
Accepted in revised form 6/21/2025

Keywords:
Pd–NHC Complexes
Sustainable Catalysis
Density Functional Theory (DFT)
Natural Bond Orbital Analysis (NBO)

ABSTRACT

A density functional theory (DFT) study was performed to investigate the structural and electronic properties of four sulfonated, water-soluble PEPPSI–Pd–NHC complexes (2a–2d). All complexes were fully optimized, followed by higher-level single-point calculations to obtain an accurate description of their electronic structures. Metal–ligand interaction energies were evaluated to assess the strength and stability of the Pd–NHC bonding. Natural Bond Orbital (NBO) and Energy Decomposition Analysis (EDA) were employed to analyze charge distribution, bonding characteristics, and the nature of Pd–ligand interactions. The results reveal that variations in the NHC ligands significantly influence the electronic environment of the Palladium center. Notably, the catalyst bearing a 2,6-diisopropylphenyl substituent exhibits the strongest metal–ligand interaction, in good agreement with its superior experimental performance.



1. Introduction

Transition-metal-catalyzed methodologies for carbon–carbon bond formation play a central role in modern organic synthesis [1–3]. The development of efficient, robust, and sustainable palladium catalysts remains an active area of research, especially in the context of green chemistry and industrial applicability [4-6].

N-heterocyclic carbene (NHC) ligands have emerged as privileged ligands in palladium catalysis owing to their strong σ-donating ability, tunable steric properties, and high resistance toward oxidative degradation [7-10]. PEPPSI-type Pd–NHC complexes, in particular, have shown remarkable catalytic activity and stability in various cross-coupling reactions, including Suzuki–Miyaura processes [11-13]. PEPPSI type Pd–NHC catalysts have been widely explored due to their air and moisture stable nature, operational simplicity, and broad applicability in carbon–carbon bond–forming reactions. These complexes often outperform traditional Pd/phosphine systems in Suzuki–Miyaura and related cross coupling reactions, making them valuable tools in both academic and applied synthesis [14].

Despite extensive experimental investigations, a detailed molecular-level understanding of the electronic structure, metal–ligand bonding, and charge transfer processes in these catalysts remains limited [15-17]. Computational chemistry, particularly density functional theory (DFT), provides a powerful framework to elucidate such effects and to rationalize experimentally observed trends in catalytic activity [18-20]. Methods such as Natural Bond Orbital (NBO) analysis and Energy Decomposition Analysis combined with Natural Orbitals for Chemical Valence (EDA–NOCV) enable a quantitative description of charge distribution, donor–acceptor interactions, and the nature of metal–ligand bonding [21–24].

In this work, a theoretical investigation is presented on the bonding characteristics and the nature of the Pd–L interactions in four Pd–NHC

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URL: https://jeecpjournal.com/index.php/jeecp/article/view/25

Please cite this article as: : Alavipour, E., & Bayat, M., (2025). *Journal of Enviromental Economics & Chemical Processes (JEECP)*, *2*(3), 96-99.

catalysts that were previously prepared experimentally [25]. Geometry optimizations, electronic structure analyses, natural bond orbital (NBO) natural charge, charge-transfer and donor-acceptor interaction [26-28] evaluations, along with energy decomposition analysis combined with natural orbitals for chemical valence (EDA–NOCV), were carried out to gain detailed insight into the structural and electronic factors governing catalyst stability and reactivity. The results provide a coherent theoretical interpretation of the experimental observations and contribute to the rational design of improved Pd–NHC catalysts for sustainable cross-coupling chemistry.

2. Computational Details

All quantum chemical calculations were carried out using density functional theory (DFT). Geometry optimizations for all four Palladium–NHC catalysts were performed using the BP86 exchange–correlation functional, which has been shown to provide reliable geometries for transition-metal complexes [29-30]. The def2-SVP basis set was employed for all atoms during geometry optimization. No symmetry constraints were imposed during the optimization process, and all optimized structures were confirmed to be true minima by vibrational frequency calculations, exhibiting no imaginary frequencies.

Single-point energy calculations were subsequently carried out on the optimized geometries at a higher level of theory using the BP86 functional in conjunction with the def2-TZVP basis set in order to obtain more accurate electronic energies.

Natural Bond Orbital (NBO) analyses were performed on the optimized structures to evaluate natural atomic charges and charge-transfer processes between the palladium center and the ligands. Charge-transfer values were extracted to quantify electron donation and back-donation effects within the complexes. In addition, second-order perturbation theory within the NBO framework was used to identify and analyze the most significant donor–acceptor interactions.

Energy Decomposition Analysis combined with Natural Orbitals for Chemical Valence (EDA–NOCV) was carried out to dissect the metal–ligand interactions into physically meaningful components, including electrostatic, Pauli repulsion, and orbital interaction terms. The NOCV analysis further allowed visualization and quantification of the dominant charge-flow channels between palladium and the NHC ligands.

3. Results and Discussion

Structural Analysis

The optimized geometries of all four Pd–NHC catalysts reveal a square-planar coordination environment around the palladium center, consistent with experimentally proposed structures. The Pd–C(NHC) bond lengths obtained at the BP86/def2-SVP level fall within the typical range reported for PEPPSI-type complexes. Results are shown at (Figure 1), indicating strong metal–carbene interactions. Single-point energy calculations at the BP86/def2-TZVP// BP86/def2-SVP level confirm the relative energetic stability of the optimized structures and provide a reliable basis for subsequent electronic analyses.

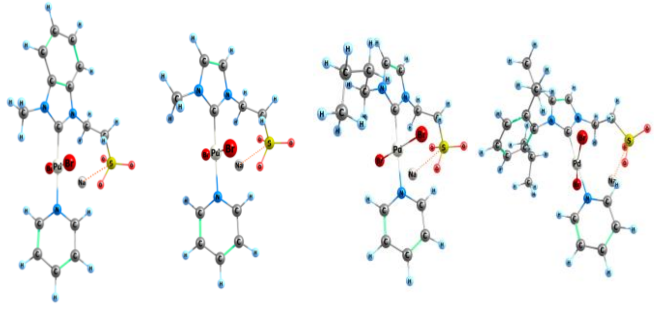
Pd(2A) Pd(2B) Pd(2C) Pd(2D)

Figure 1: Optimized structures of the Pd–NHC complexes calculated at the BP86/def2-SVP level of theory.

NBO Analysis

NBO analysis was performed to evaluate natural charges, charge transfer and key donor–acceptor interactions, providing insight into electron donation and back-donation within the Pd–NHC complexes.

NBO analysis at the BP86/def2-TZVP//BP86/def2-SVP level of theory, reveals pronounced charge redistribution upon coordination of the NHC ligands to the palladium center. The natural charge on Pd is reduced relative to the formal Pd(II) description, indicating substantial electron donation from the ligands. Charge-transfer analysis identifies the carbene carbon as the dominant electron donor, with additional contributions arising from ancillary ligands. Catalysts bearing more strongly electron-donating substituents exhibit increased electron density at the palladium center. The calculated natural charges and charge-transfer values are summarized in Table 1.

Table 1. Natural charges and charge-transfer values for Pd and ligands calculated via NBO in [Pd-L] complexes.

Catalyst	Natural Charge		Charge Transfer (e)
	Pd	L	
Pd (2A)	0.19	-0.19	-1.81
Pd (2B)	0.30	-0.30	-1.70
Pd (2C)	0.16	-0.16	-1.84
Pd (2D)	0.86	-0.86	-1.14

Second-order perturbation analysis highlights the most important donor–acceptor interactions governing metal–ligand bonding. The dominant interaction corresponds to σ-donation from the filled lone-pair orbital of the carbene carbon into the empty palladium d-orbitals. Additional stabilization arises from back-donation from filled palladium d-orbitals into antibonding orbitals of the ligands. The magnitude of these interactions varies among the catalysts and provides a quantitative explanation for differences in metal–ligand bond strength and electronic flexibility (See Table 2).

Table 2. Most important values Donor−Acceptor interactions analysis (kcal/mol) of [Pd-L] complexes calculated via NBO

Donor Acceptor	Type	Catalyst			
		Pd(2A)	Pd(2B)	Pd(2C)	Pd(2D)
N–C$_{(NHC)}$→Pd	σ→LP*	3.11	3.04	3.12	3.11
N$_{(Pyr)}$→Pd–C$_{(NHC)}$	LP→LP*	30.67	37.7	35.22	24.98
N$_{(Pyr)}$→Pd	σ→LP*	9.70	9.60	9.59	7.86
Pd→C$_{(NHC)}$	LP→ σ*	10.80	10.03	9.71	9.42
Br1→Pd	LP→LP*	6.78	5.79	5.57	5.44
Br2→Pd	LP*→σ*	4.06	4.08	4.13	---

EDA–NOCV Analysis

Energy Decomposition Analysis was performed at BP86-D3/TZ2P to dissect the interaction between the palladium center (Fragment A) and the remaining ligands (Fragment B) of the four Pd–NHC complexes. The total interaction energy ΔEint is predominantly stabilizing for all complexes, ranging from –193.97 to –200.71 kcal·mol^{-1}. Decomposition into physically meaningful components shows that the orbital interaction term ΔEorb contributes significantly (36–42%) to the overall stabilization, highlighting the importance of covalent metal–ligand bonding. Electrostatic interactions (ΔEelstat) are also substantial, accounting for 56–60% of the total attractive energy, whereas dispersion effects (ΔEdis) play a minor yet non-negligible role (2–4%). Among the four catalysts, Pd(2D) exhibits the most stabilizing total interaction (ΔEint = –200.71 kcal·mol^{-1}) with a slightly larger orbital contribution compared to the others, suggesting a stronger covalent character of the Pd–ligand bonding between the complexes investigated here. These results indicate that both electrostatic and orbital interactions synergistically govern the stability of Pd–NHC complexes, while dispersion and steric repulsion modulate the fine electronic structure of the metal–ligand framework (See Table 3).

Table 3. Calculated EDA (energy decomposition Analysis)(kcal/mol) for [Pd-L] complexes

	ΔE_{int}	ΔE_{dis}	ΔE_{orb}	ΔE_{elast}	ΔE_{pauli}
Pd(2A)	-198.28	-9.40(4%)	-232.69(37%)	-309.20(59%)	-353.10
Pd(2B)	-193.97	-9.63(2%)	-226.34(42%)	-304.94(56%)	-346.94
Pd(2C)	-198.94	-9.97(4%)	-231.10(36%)	-305.14(60%)	-347.28
Pd(2D)	-200.71	-11.70(3%)	-225.30(41%)	-288.68(56%)	-324.98

Natural Orbitals for Chemical Valence (NOCV) analysis was performed to visualize and quantify the donor–acceptor interactions between the palladium center and the ligands. As shown in Figure 2, the first deformation density ($\Delta\rho_1$) represents electron flow from the palladium center toward the carbene, the pyridine, and the two bromine atoms, indicating partial back-donation from the metal. In the reverse direction ($\Delta\rho_2$), significant electron donation from the lone pair of carbene carbon, pyridine nitrogen, and bromine atoms toward the palladium center is observed, highlighting the dominant σ-donor character of the ligands. A third component ($\Delta\rho_3$) shows minor electron transfer from palladium to the carbene and pyridine carbons, reflecting subtle π-back-donation contributions.

These results confirm that the Pd–NHC bonding is governed primarily by ligand-to-metal electron donation, with additional, smaller metal-to-ligand back-donation components, and provide a clear visual representation of the electronic interactions stabilizing the complexes (See Figure 2).

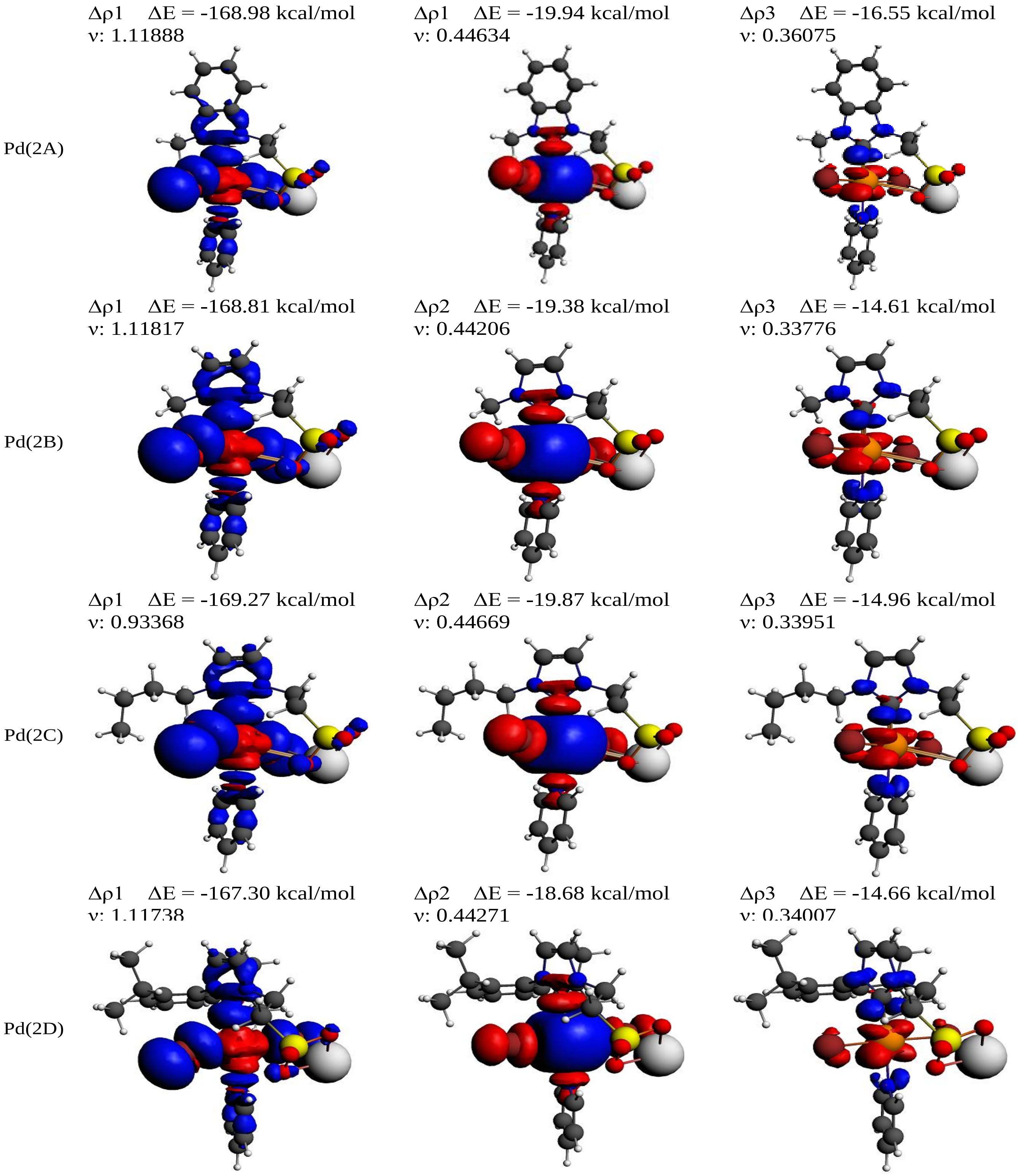

Figure 2. NOCV deformation densities for the Pd–NHC complexes. Red → blue indicates electron flow, illustrating ligand-to-metal donation and metal-to-ligand back-donation.

4. Conclusions

Density functional theory (DFT) analyses of four Pd–NHC catalysts elucidate the electronic structure and nature of Pd–L bonding. Natural bond orbital (NBO) results identify the carbene carbon as the principal electron donor, with ancillary ligands contributing additional electron density and inducing significant charge redistribution at the palladium center. Energy decomposition analysis (EDA) indicates that electrostatic and orbital interactions dominate the stabilization of the Pd–NHC bond, whereas dispersion interactions play a minor role. Natural orbitals for chemical valence (NOCV) analysis confirms strong ligand-to-metal σ-donation accompanied by weaker metal-to-ligand back-donation, highlighting the synergistic character of Pd–NHC interactions. Theoretical results are in good agreement with experimental data for all complexes except Pd(2D), which exhibits slightly stronger interaction energies and enhanced covalent character. These findings demonstrate that subtle ligand modifications can effectively tune metal–ligand interactions and provide fundamental insight for the rational design of more efficient and electronically adjustable sustainable water-soluble palladium catalysts for cross-coupling reactions.

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