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Research Article

DFT INVESTIGATION OF TRANSTION METALS ARENE COMPOUNDS WITH FUNCTIONALIZED IONIC LIQUID

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Abstract: *Electrochemical properties and theoretical DFT computations have been carried out for the cationic parts of complexes of ionic liquid-based phosphinite, (**1A-3A**). The effects of the chemical structures of cationic parts of three complexes were examined in relation to the variable property of electron-donating ligands for ruthenium and iridium complexes were determined. Their potential energy surfaces in the ground state, electronic densities, and also frontier orbitals HOMO and LUMO have been obtained via DFT calculations. It has been shown that DFT calculations can successfully be used for exploring electrochemical properties of cations, which includes transition metals. It was revealed that complex **1A** is the chemically softest molecule, while complex **2A** is the most electrophilic one.*

Keywords*: Ionic Liquid, HOMO-LUMO, DFT calculation, Iridium, Ruthenium.*

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1. Introduction

Computer-based theoretical calculations have become a crucial tool, especially in the last decades [1]. Many theoretical techniques, such as Density Functional Theory (DFT) ab-initio methods, molecular mechanics simulations, and some quasi-experimental methods are often used to study molecular properties in several fields such as pharmacology and materials engineering [2]. Among them, Density Functional Theory (DFT), has proved itself the most effective approach for many chemical calculations, such as optimizing molecular structures, obtaining molecular electrostatic potential (MEP), total electron densities, and energy levels of frontier orbitals (HOMO and LUMO) and also chemical descriptors including chemical hardness, electrophilicity, electronegativity, and chemical potential [3,4,5,6]. Furthermore, DFT technique is also preferred due to its computationally low costs and relatively high performance [1,3].

Within this perspective, we have started to study transition metal complexes containing phosphinite moiety with imidazolium ionic liquids, in order to understand the electrochemical behavior of transition metal complexes of phosphinites better and perform the theoretical calculations of such complexes [7]. In this study, DFT studies of cationic parts of previously synthesized Ru(II)- and Ir(III)-phosphinite compounds based on ionic liquid were reported. Also, the impacts of the chemical constructions of three phosphinite complexes were selected in relation to the variable property of η^6-p-cymene, η^6-benzene and η^5-C_5Me_5 substituent for **1A**, **2A** and **3A**, respectively and determined their potential energy levels and induced levels HOMO and LUMO. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels were computed by DFT approach.

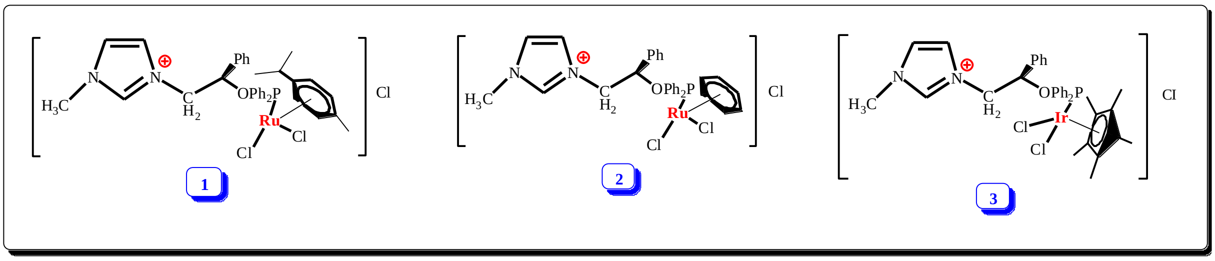
2. Experimental Computational method

All calculations were performed by using DFT (Density Functional Theory) approach. GAMESS (the General Atomic and Molecular Electronic Structure System), which is a general *ab initio* quantum chemistry package, was used for calculations [1,8]. The exchange-correlation functional for calculations was the hybrid Becke, three-parameter, Lee-Yang–Parr, using the coulomb attenuating method (CAM-B3LYP) [9]. And also, the SBKJ (Stevens, Bash, Krauss, Jasien) valance basis set was used with ECP (Effective Core Potential) [10]. There were no imaginary frequencies for any cases, therefore it is confirmed that the optimized molecular structures correspond to real minims on the PES (Potential Energy Surface).

3. Results and Discussion

3.1. DFT Study

DFT method was used to unravel the electrochemical behavior of cationic parts of previously prepared complexes **1-3** (Scheme 1) [11]. Since outer chlorine atom moves freely in the solution, it was excluded in the calculations, and the remaining positively charged part **(1A-3A)** was taken into account.



Scheme 1. [3-[(2R)-2-({[dichloro(η^6-p-cymene)ruthenium]diphenyl phosphanyl}oxy)-2-phenylethyl] -1-methyl-1H-imidazol-3-ium chloride]] **(1),** [3-[(2R)-2-({[dichloro(η^6-benzene)ruthenium] diphenylphosphanyl}oxy)-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride]] **(2),** [3-[(2R)-2-{[(dichloro(η^5–pentamethylcyclopentadienyl)iridium) diphenyl phosphanyl]oxy}-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride]] **(3).**

The optimized molecular structures of cationic parts (**1A-3A)** of complexes **1-3** have been given in Figure 1. As known, optimized molecular structure of a molecule represents the minimal energy conformation of the molecule, and that's why it is important [12].

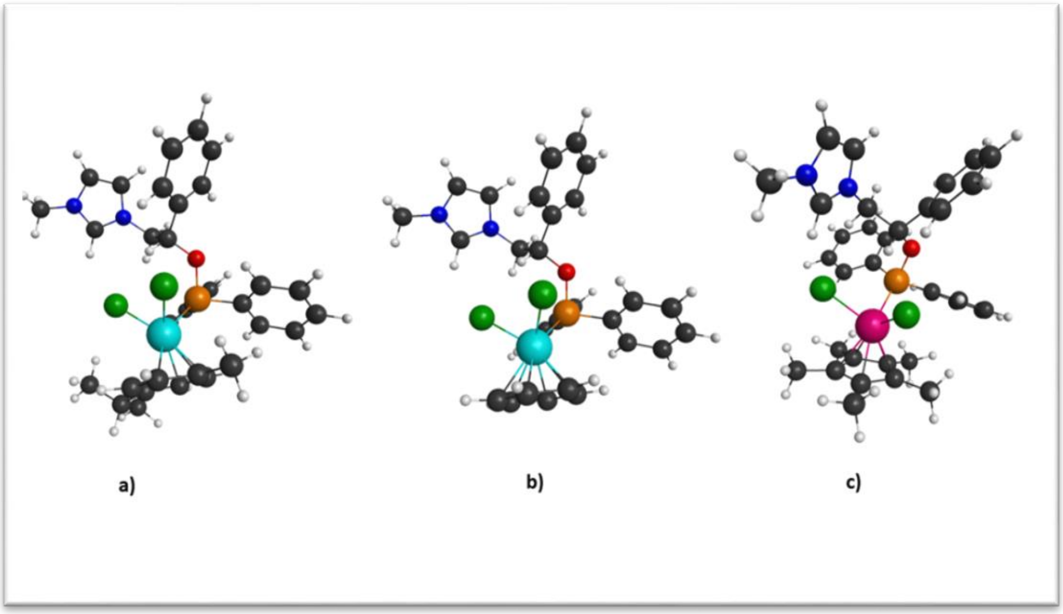


Figure 1. The optimized molecular structure of (a) **1A**, (b) **2A**, and (c) **3A**.

The molecular electrostatic potential (MEP) is helpful to investigate the molecular features including hydrogen bonding, and nucleophilic and electrophilic attacks on the molecule site [13,14]. Since the MEP is basically a three-dimensional map that gives the electrostatic potential for every point all around the molecule, it is a very fruitful source of information to estimate how the molecule responds to other molecules in any possible cases. For instance, it can be used to estimate both possible locations and relative intensities of both nucleophilic and electrophilic attacks by other molecules [15]. The reactivity of molecules can also be predicted by visual inspection of different colors, which represent different values of the MEP [16,17]. The red color corresponds to the positive potential regions, which are localized over the hydrogen atoms, whereas the blue color indicates the high electron density as well as negative potential regions, which are localized over the electronegative atoms (nitrogen, oxygen) [18,19]. As seen in Figure 2**, 1A-3A** have dominant positive potential, therefore their MEPs are almost fully red, as expected because they are actually positively charged cations.

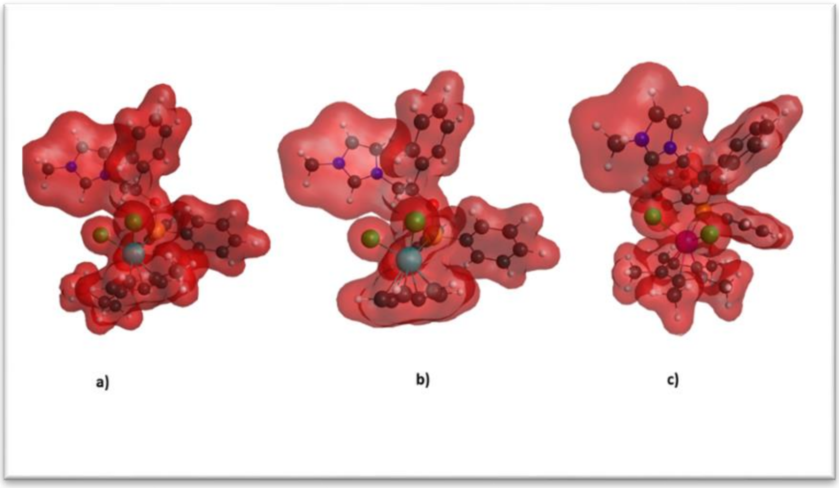


Figure 2. The molecular electrostatic potential of (a) **1A**, (b) **2A**, and (c) **3A**.

As known, the total electronic density is a graph of quantum mechanics probabilities of finding electrons at every given point. It can give us a strong insight into molecules' overall and local polarization. Information on electronic densities also can help to interpret the behavior of the molecule in chemical interactions [20-22]. As it can be seen in Figure 3**,** while there are no big differences in electronic densities around each atom, still electrons can be found slightly denser around oxygen and chlorine atoms.

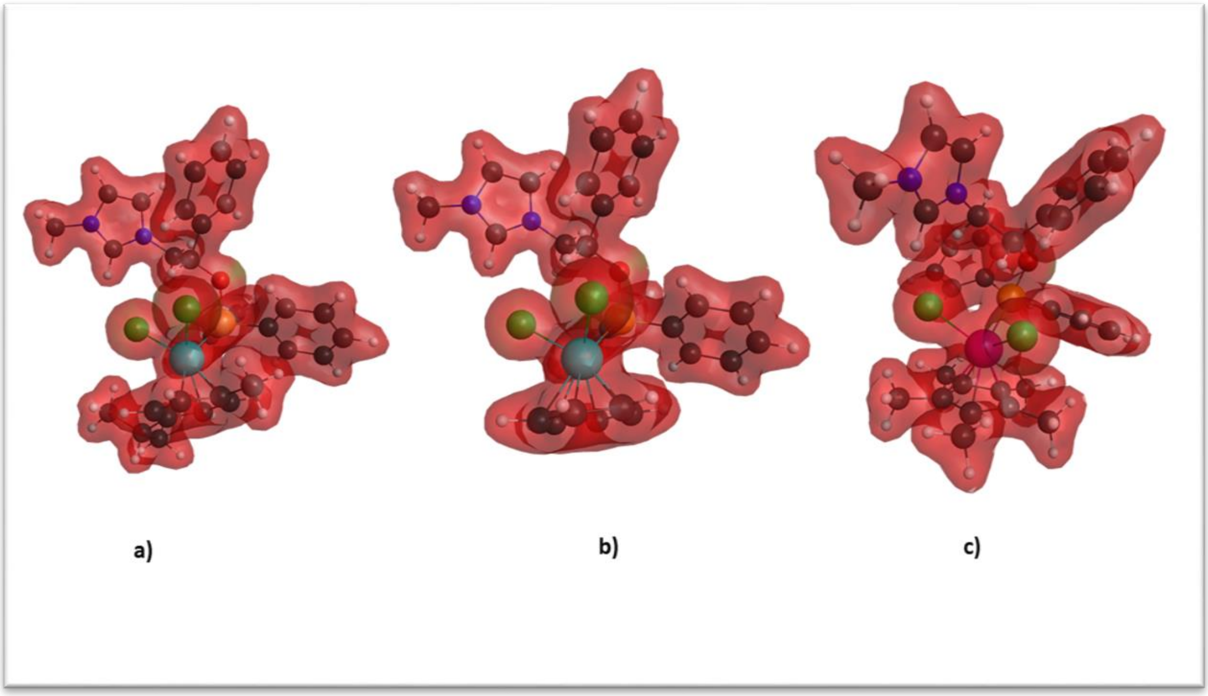


Figure 3. The total electron density of (a) **1A**, (b) **2A**, and (c) **3A**.

Molecular orbital analysis is crucial in establishing the compound's electrical and optical characteristics, as well as its chemical reactions [23]. The energies of HOMOs and LUMOs of **1A-3A** are given in **Figure 4** and Table 1. A substantial E_{HOMO} value indicates a higher ability to donate electrons, whereas a lower E_{LUMO} value shows a higher tendency to accept electrons [17, 24]. The calculated HOMO energy values tabulated in Table 3 are -9.3607 eV, -9.5784 eV, and -9.4968- eV, for **1A-3A**, respectively. Thus, the ability of **3A** to donate electrons is lower than **1A**, but it is higher than that of **2A**. LUMO energy values of **1A-2A** were found as -2.8028 eV, -2.9116 eV, and -2.6395 eV, respectively. On the contrary, the ability of **1A** to accept electrons is lower than **2A**, but it is higher than that of **3A**. When ΔE values for cationic parts of these complexes were considered, it was observed that they were 6.5579, 6.6668, and 6.8573 eV, respectively (Figure 1 and Table 1), implying that the complexes are rather stable. If we compare ΔE values for the cationic parts of complexes with each other, we realize that the energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$) of **1A** is smaller, leading to lower kinetic stability and a higher chemical reactivity than those of **2A** and **3A** [17,25]. Furthermore, considering the type of transition metal in **Figure 4**, one can conclude that cationic parts of Ru(II) complexes **1A** and **2A** are more reactive than those of Ir(III) complex **3A**.

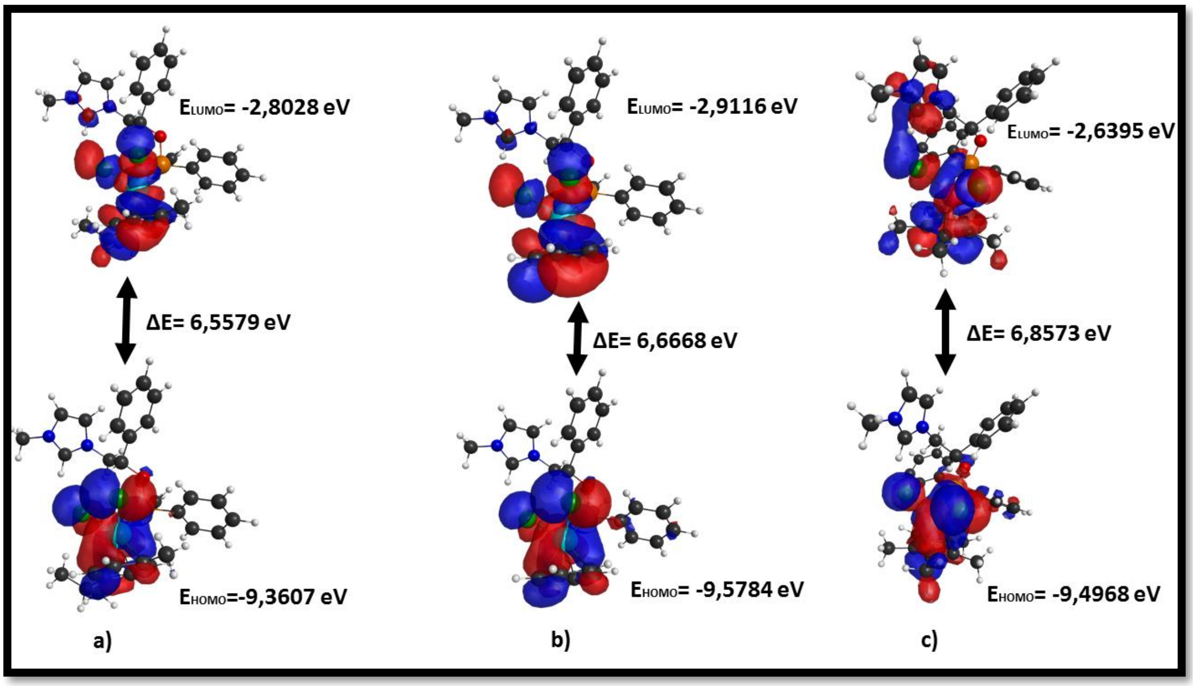


Figure 4. Frontier molecular orbitals (HOMO-LUMO) of **1A-3A** calculated by DFT.

The calculated chemical descriptors for **1A-3A**, χ (electronegativity), η (chemical hardness), ω (electrophilicity), S (softness), and μ (chemical potential) have been given in Table 1 and Figures 5-7. A big ΔE indicates a hard molecule, whereas a small ΔE indicates a soft molecule. Because they could easily supply electrons to an acceptor, soft molecules are more reactive than hard ones [23]. When we look at Figure 5, we see that the hardness of **1A** is lower (softness is higher, Table 1), since it has a lower ΔE value, implying that it is more reactive than the other cationic parts of complexes. Electrophilicity is the other theoretical descriptor that can be used to make a comment about the electron-accepting tendency of a molecule [17, 26]. The electrophilicity indexes of the presented **1A-3A** are 5.6402 eV, 5.8499 eV, and 5.3698 eV respectively, as seen in Figure 6. Electrophilicity indexes of **2A** are higher than that of **1A** and **3A**, indicating that it has the strongest electrophilic character. As DFT calculations showed, **2A** is also the most electronegative one (χ:6.2450 eV, Figure 7, Table 1). Then, its chemical potential becomes -6.2450 eV (Table 1), because chemical potential (μ) is the negative of electronegativity [14].

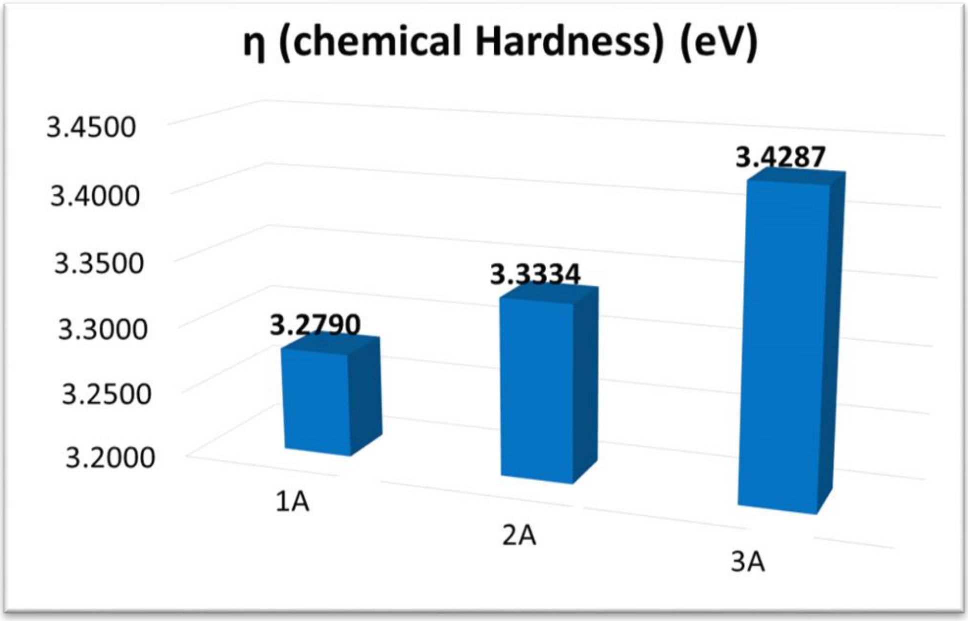


Figure 5. The calculated η (chemical Hardness) values of **1A-3A.**

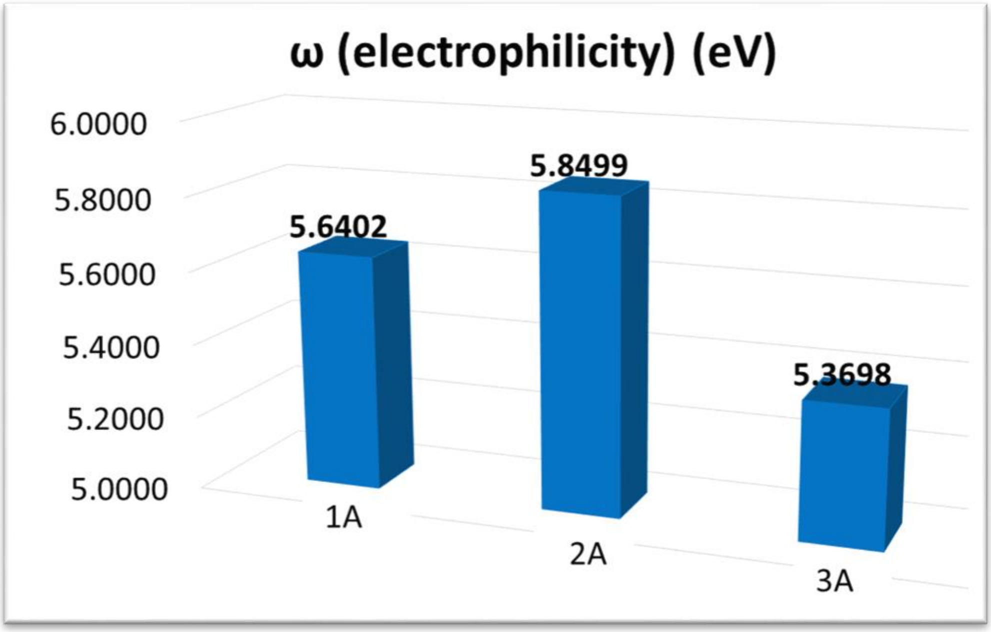


Figure 6. The computed ω (electrophilicity) values of **1A-3A.**

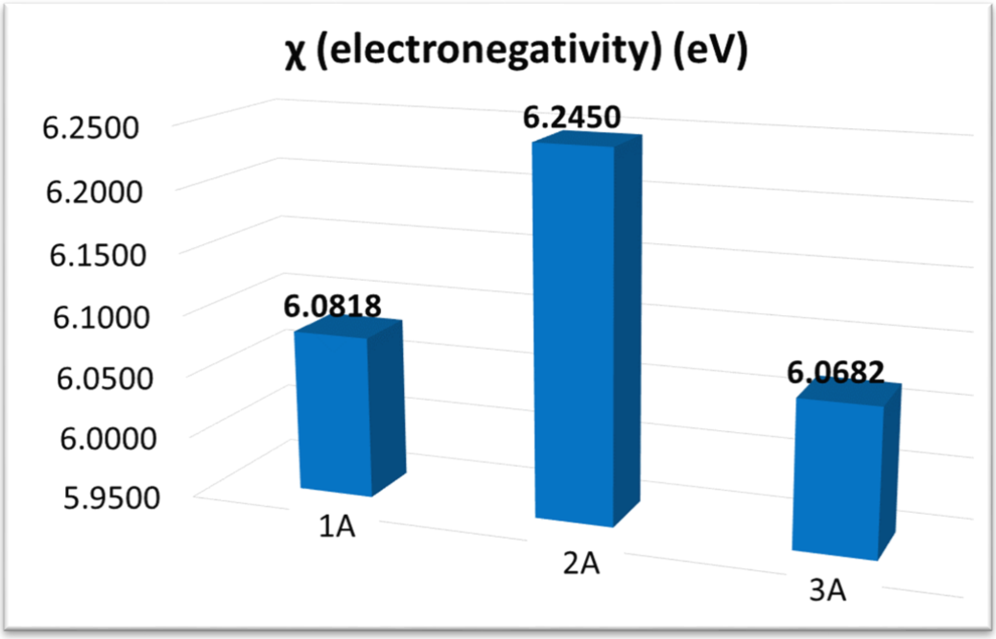


Figure 7. The calculated χ (electronegativity) values of **1A-3A.**

Table 1. The calculated E_{HOMO}, E_{LUMO}, ΔE, and chemical descriptors (η (chemical hardness), S (softness), ω (electrophilicity), χ (electronegativity) and μ (chemical potential)) for cationic parts of complexes **1A-3A**.

Molecules	$E_{(HOMO)}$ (eV)	$E_{(LUMO)}$ (eV)	ΔE (eV)	η (eV)	S (eV^{-1})	ω (eV)	χ (eV)	μ (eV)
1A	-9.3607	-2.8028	6.5579	3.2790	0.3050	5.6402	6.0818	-6.0818
2A	-9.5784	-2.9116	6.6668	3.3334	0.3000	5.8499	6.2450	-6.2450
3A	-9.4968	-2.6395	6.8573	3.4287	0.2917	5.3698	6.0682	-6.0682

4. Conclusion and Perspectives

In conclusion, the molecular structure of the complexes of an ionic liquid-based chiral phosphinite ligand was successfully examined by using the Density Functional Theory (DFT). Molecular electrostatic potential and total electron density of cationic parts of the studied complexes indicated the existence of proper sites to attack electrophilic and nucleophilic substances. Calculated $E_{(HOMO)}$ & $E_{(LUMO)}$ values for three cationic substances are in line with the expectations for free cationic structures. We can see that $E_{(HOMO)}$ values are deep below zero (around -9.5 eV) while $E_{(LUMO)}$ values also meaningfully deeper than zero eV (around -2.8 eV). The lowest energy gap (ΔE) for **1A** means that it is expected to behave chemically more reactive than **2A** and **3A** in solution as softer cation. On the other hand, **2A** is the most electrophilic and the most electronegative one, therefore it is more likely become an effective target for nucleophilic attacks. Thus, as a main conclusion, we can say that according to fruitful DFT calculations, we gained further useful insight into the electrochemical behavior of the complexes.

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The Declaration of Ethics Committee Approval

The authors declare that this document does not require an ethics committee approval or any special permission. Our study does not cause any harm to the environment.

Declaration of Competing Interest

The authors declare no potential conflicts of interest related to the research, authorship, and publication of this article.

Authors' Contributions

N.M: Conceptualization, Methodology, Formal analysis, Writing - Original draft preparation (20%).
N. E. B: Methodology, Resources, Investigation, Visualization (20%).
C.K: Data curation, Visualization, Investigation, Methodology (20%).
V.B: Conceptualization, Software, Methodology, Investigation (20%).
M.A: Conceptualization, Supervision, Validation, Funding acquisition (20%).
All authors read and approved the final manuscript.

The compliance to research and publication ethics:

This study was performed by complying research and ethics rules.

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