Theses of Doctoral (PhD) Dissertation

Exploring the catalytic role of noble metal complexes: DFT based mechanistic studies

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I. INTRODUCTION AND GOALS

The transition metal catalysed homogeneous catalysis is an exciting area of research form both experimental and theoretical points of view. Nowadays, the complexes that activate H–H and C–H bonds are not only used in hydrogenation or coupling reactions, but they are "reinvented" as catalysts in hydrogen storage systems. These complexes and the reaction conditions developed over the years clearly present a baffling amount of information. Therefore, employing computational modelling to explain the underlying general mechanisms and estimate the properties of novel catalysts seem indispensable. Among the computational methods the density functional theory is the most commonly used method, with its application becoming a research field of its own over the last couple of decades.

The development of noble metal complexes containing phosphine ligands has been a long-standing project of the Research Group of Homogeneous Catalysis at the Department of Physical Chemistry. The group has designed numerous catalysts that show a wide range of solubility (mostly water), selectivity and kinetic properties. For example, the selective hydrogenation of an α,β-unsaturated carbonyl compound needs a careful determination of the proper catalyst which is not a trivial task to perform. Furthermore, the aqueous medium can also play an important role; it not only makes the reaction "greener", but the

water molecules might explicitly play a role in the mechanism by opening new reaction pathways.

At the start of my work there were a large amount of experimental results available and my goal was to understand the processes and propose plausible catalytic mechanisms using a computational approach. I also present new experimental results beyond the DFT calculations. These measurements were conducted by others and therefore I refer to these results in first person plural and do not go into details about the applied device and techniques. It is also worth mentioning that these new experiments were performed to explain questions raised from the calculations and not the other way. Therefore, they are an essential part of my work.

II. APPLIED METHODS

The DFT calculations were performed using the Gaussian 09 software package which is accessible on the Hungarian supercomputing infrastructure. Most of the CPU time was used on the Debrecen 2 (Leo) supercomputer. In the theoretical model, the dispersion corrected B3LYP-D3 functional was chosen. For the non-metallic atoms, the TZVP basis set, while for the metal centres the CRENBL effective core potential with the corresponding valance basis was employed. The PCM method was used to account for solvation which has many deficiencies and possible corrections, among which I present one in the dissertation. The intermediate and transition state geometries were found after performing geometry optimizations, then verified using frequency calculations at the same level of theory. The reported energy values are relative Gibbs free energies at 298.15 Kelvins and 1 atm pressure. In the first part of my work, I perform functional testing and TDDFT calculations, but the rest of the model remains the same as above.

III. LIST OF ABBREVIATIONS

DFT	Density Functional Theory
ARS	Alizarin Red S
TDDFT	Time Dependent DFT
emim	1-ethyl-3-methylimidazolium (ion)
COD	1,5-cyclooctadiene
***m*tppts**	monosulfonated triphenylphosphine
***m*tppms**	trisulfonated triphenylphosphine
„phosphine", P	In my thesis the *m*tppms and *m*tpps ligands were simplified to PPh_3 by omitting the sulfonate groups. The general notation on the left may refer to any of these particles based on the context.
NHC	*N*-heterocyclic cabene
cinnamaldehyde	(2E)-3-Phenylprop-2-enal
TOF	Turnover frequency

IV. NOVEL SCIETIFIC RESULTS

Study of ARS and its palladium complex

1. I have determined that the M06 is the most suitable functional among the B3LYP, BH&HLYP, CAM-B3LYP, LC-ωPBE, M062X, PBE0 and ωB97-XD functionals for the study of ARS. The tests were performed on the mono-, di- and trianonic forms of ARS with the aim to find the functional that best reproduces the characteristic UV-visible absorption band of each species. I have performed a conformational analysis to find the most stable isomer of each protonated form then compared the spectra obtained from my calculations to the experimental data. The mean errors (ME) and mean absolute errors (MAE) of the main absorption wavelengths are shown in Fig. 1.

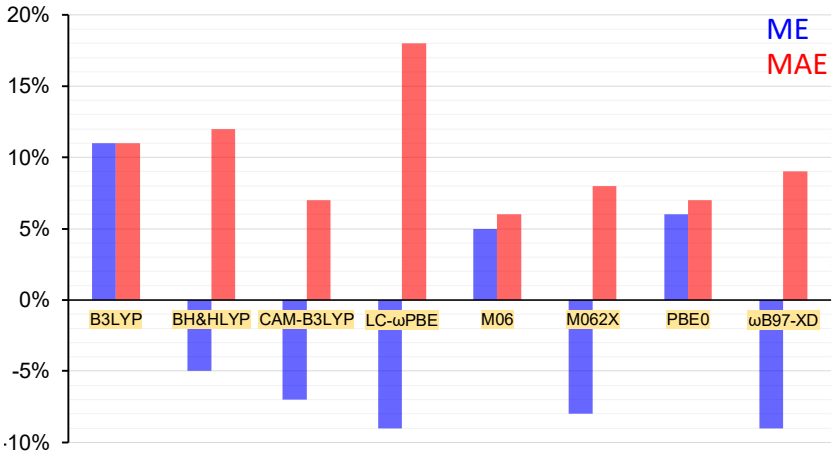

Figure 1. The result of the functional testing.

2. I have performed the spectrum to structure assignment of the protonated and deprotonated $Pd(ARS)_2$ complex. The results indicate that the protonated complex prefers the hydroxy-keto binding in contrast to the deprotonated form where the catechol coordination is favoured. The proposed structures together with the calculated and newly measured spectra are shown in Fig. 2.

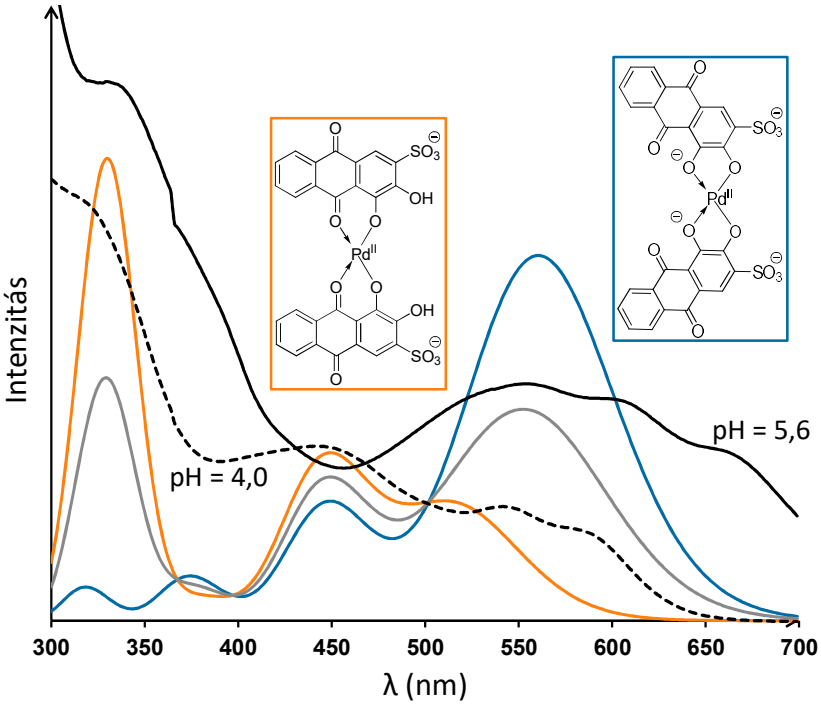

Figure 2. The proposed structures of $Pd(ARS)_2$ in the protonated and deprotonated states together with their calculated (coloured) and newly measured (black) UV-vis spectra.

3. I have determined that the ARS ligand in the palladium complex can also act as a substrate in hydrogenation reactions where the ARS is saturated on the ring that does not bear −OH groups. Hydroquinone derivatives may also form, but only after the saturation of the ring.
4. I have determined that the L, ML and ML_2 species with reduced ARS ligands have very similar UV-vis spectra, therefore the TDDFT aided spectrum to structure assignment method I employed above cannot separate them.

Hydrogen storage in the formate-bicarbonate system: study of the [Ir(emim)(η^4-COD)(*m*tppts)]$^+$ catalyst

5. Using DFT calculations, I have shown that from the [Ir(emim)(η^4-COD)(mtppts)]$^+$ complex, the least strongly bound COD ligand needs to dissociate in order to form the active catalyst. We have proven this assumption experimentally with ^{13}C NMR.
6. Using DFT calculations, I have shown that in the presence of excess phosphine the coordinated COD can be replaced with phosphine yielding the [IrP_2(NHC)(HCOO)] complex. I have also shown that in this complex the intramolecular C−H activation of the NHC ligand is blocked kinetically. This is in accordance with the previous experimental results.
7. Using DFT calculations, I have shown that without excess phosphine, the coordinated COD can be hydrogenated in an exergonic process yielding monophosphine complexes where the intramolecular C−H activation of the NHC ligand is possible. We have proven the existence of the monophosphine complex using ^{13}C NMR. As shown in Fig. 3, we have also observed deuterium exchange in the *N*-methyl end groups,

indicating the activation of the NHC, when the Na_2[Ir(COD)(emim)(*m*tppts)] complex was dissolved in DMSO:D_2O = 1:5 mixture. After adding 5 equivalents of $H^{13}COONa$, the quartet signal of the methyl carbon becomes more elaborate indicating the coupling with the higher spin deuterium atoms.

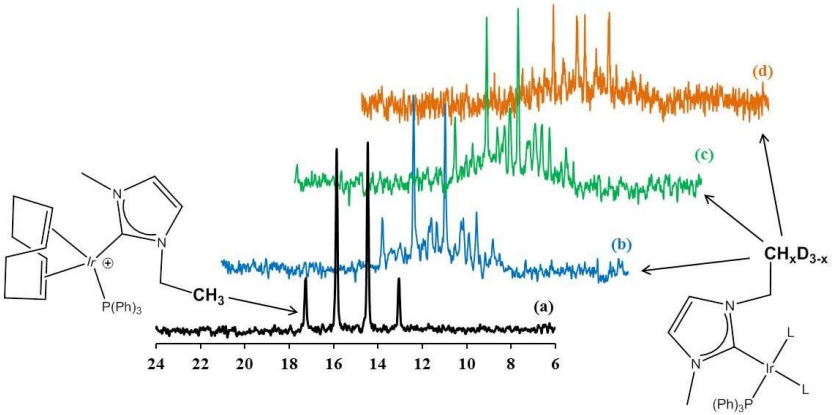

Figure 3. ^{13}C NMR spectra of the Na_2[Ir(cod)(emim)(*m*tppts)] complex dissolved in DMSO:D_2O (1:5) mixture. (a) without formate, (b, c, d) after adding 5 equivalents of $H^{13}COONa$. (**b**): t = 24 h; (**c**): t = 48 h; (**d**): t = 168 h

8. I have developed a catalytic cycle for the catalysis of the formate-bicarbonate equilibrium. The result is shown in Fig. 4 where the active species are the iridacycles formed in the monophosphine complex after the intramolecular C−H activation of the NHC ligand. This mechanism is most likely the cause of the observed deuterium exchange, however further calculations suggest that it is not the main cycle responsible for hydrogen storage.

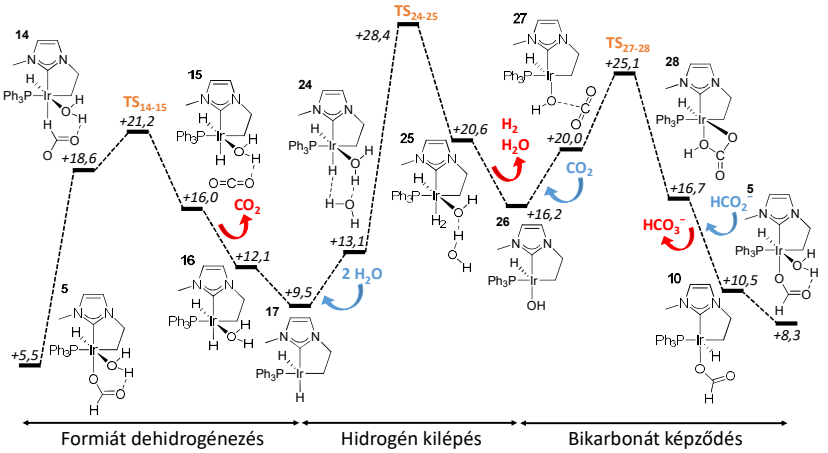

Figure 4. The free energy profile of the iridacycle mechanism.

9. I have developed a plausible catalytic cycle which is responsible for the hydrogen storage in the formate-bicarbonate equilibrium. The mechanism is shown in Fig. 5. It starts form the complex obtained after COD dissociation where the two liberated coordination sites are filled with a water molecule and a formate ion. In the first step, the oxidative addition of the solvent molecule takes place forming the active Ir(III) centre. In the next main step, the formate C−H bond is cleaved after dissociation from the κ^1-O state then reinsertion into the κ^1-H geometry. This process yields a hydride ligand and a CO_2 molecule where the latter does not leave the complex but is immediately transformed into a bicarbonate ion with the OH^- ligand formed during the water addition in the first step. After bicarbonate detachment, the *cis*-[$IrH_2P(emim)(H_2O)$] complex is obtained. In the following step, one of the hydride ligands is protonated by the solvent to yield a coordinated H_2 molecule

which is then replaced with a formate ion to recover the initial complex. The TOF determining step in the mechanism is the protonation from the solvent yielding an activation barrier of +22,4 kcal mol^{-1}. This result agrees with the activation barrier derived from literature, and with the fact that the monophosphine complex is expected to be less reactive than the thoroughly investigated diphosphine that form under phosphine excess.

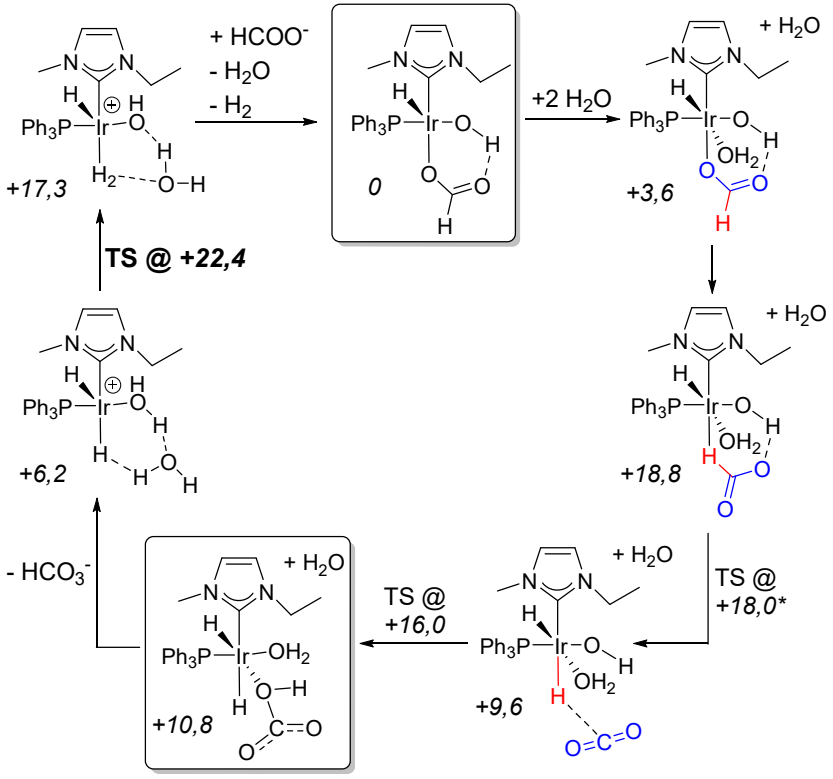

Figure 5. The simplified solvent aided catalytic cycle. *After free energy corrections, some of the TS energies fall under the corresponding minima which is due to the very flat free energy surface. The electronic energies and IRC calculations indicate proper TS's.

10. I have determined that a key feature of the main cycle discussed above is the lack of redox steps which means that the initially formed Ir(III) centre remains in the formal +3 oxidation state throughout the mechanism. All the other investigated pathways need to include an Ir(I)-Ir(III) with a corresponding barrier at least +22,4 kcal mol^{-1}.

The study of the selective hydrogenation of cinnamaldehyde catalysed by the *transz*-[Ru(II)H_2(*m*tppms)$_4$] complex

11. Using DFT calculations, I have shown that the *trans*-[RuH_2P_4] and *trans*-[$RuH_2P_3(H_2O)$] complexes have a short lifetime in water because they transform to a more stable pentacoordinate *cis*-[RuH_2P_3] form as shown in Fig. 6. I have also shown that this rearrangement cannot be blocked by coordinative saturation with a fourth phosphine or small molecules like H_2O, *i*Pr or formate. The stability of the *cis* phosphines, however, does not eliminate the possibility of a kinetically preferred *trans* hydrogenation pathway.

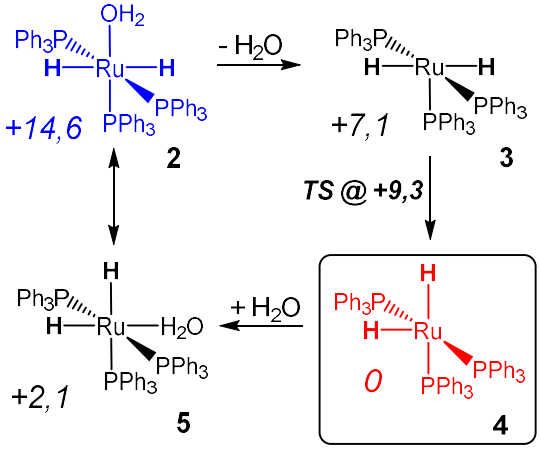

Figure 6. The possible rearrangements of the *trans*-[Ru(II)(H_2O)H_2(PPh_3)$_3$] (**2**) complex.

12. I have developed an associative mechanism which includes *trans* dihydride species. I have compared this to the analogue *cis* pathway and found that the two are kinetically equivalent within the precision of the DFT calculations. The mechanism shown in Fig. 7 starts with the coordination of the cinnamaldehyde through its carbonyl oxygen from which an alkoxy ligand is obtained via hydrid migration to the carbonyl carbon. This intermediate is the common point of the *cis* and *trans* pathways as it has an empty coordination site in the equatorial plane which contains an alkoxy, a hydride and a phosphine ligand. In the next step a hydrogen molecule enters the equatorial plane either opposite (*trans*) or next to (*cis*) the hydride ligand. The trans intermediate is more stable but the following TOF determining H−H bond cleavage is slightly more facile in the cis isomer. After this step, the product

cinnamyl alcohol is obtained together with the initial *cis* or *trans* complex.

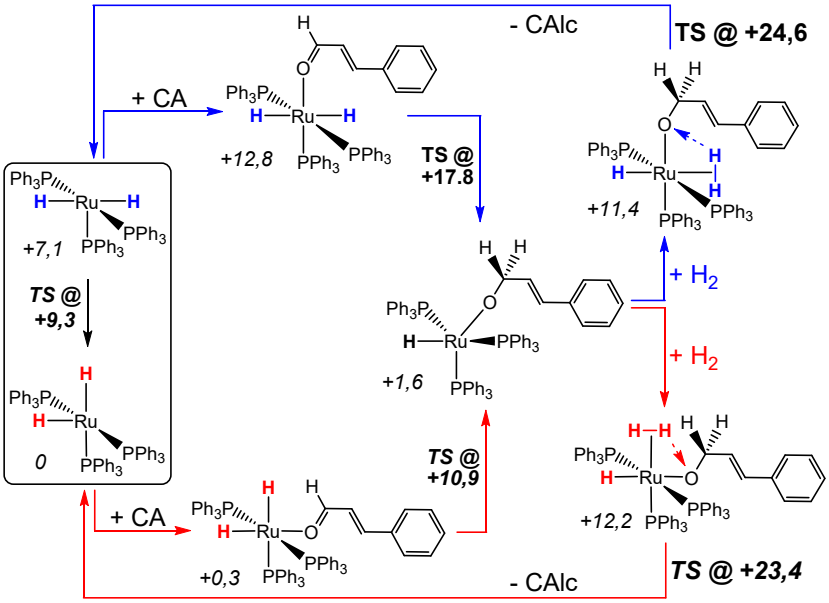

Figure 7. The simplified associative mechanism.

13. Using DFT, I have explored the effect of the solvent and found a lower energy pathway as shown in Fig. 8. The difference to the mechanism presented above is that here the alkoxy intermediate is protonated by the solvent to yield cinnamyl alcohol and an alkoxy analogue hydroxide complex from which regeneration through H_2 cleavage takes place. This pathway shows clear preference towards regeneration into the *cis* complex with an activation barrier of +20,6 kcal mol^{-1} vs. +24,8 kcal mol^{-1} calculated for the *trans* pathway.

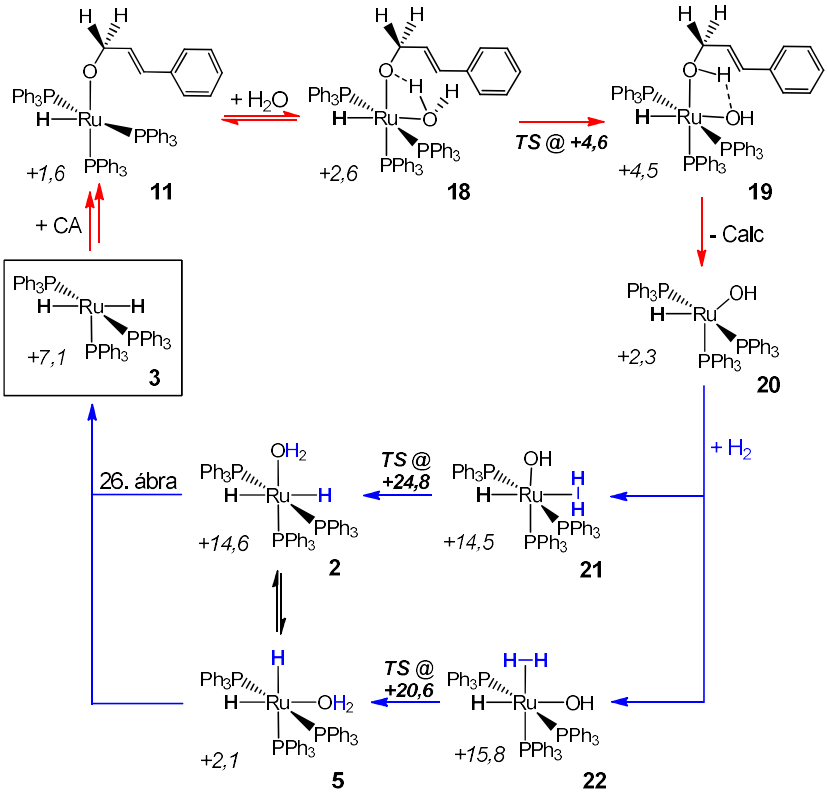

Figure 8. The simplified solvent assisted mechanism.

14. I have determined that the selectivity towards C=O hydrogenation in cinnamaldehyde is due to the steric hindrance of C=C coordination. I have developed a dissociative mechanism where the steric crowdedness is reduced in the complex by an initial phosphine dissociation. Although this way both the C=O and C=C hydrogenations proceed through a similar barrier, the highly endergonic initial step makes this pathway inferior to the associative mechanism.

15. I have investigated whether the associative mechanism is applicable to Ru(II) analogue Ir(III) and Rh(III) complexes. The replacement of the metal centre resulted in considerably higher activation barriers, indicating that such complexes follow a different hydrogenation mechanism. Therefore, I have investigated possible reductive elimination pathways (the Ru(II) mechanism retains the oxidation state of the metal) which proved to be more favourable therefore these complexes undergo a change in oxidation states.

V. POSSIBLE APPLICATIONS OF THE RESULTS

The goal of my work was to understand the mechanism of hydrogenation reactions catalysed by transition metal complexes. In the first section, the study of the ARS ligand is considered finished, but in the case of its palladium complex there are still some unanswered questions that require further experimental investigation. To interpret the new data, I expect that the computational methodology developed here will be an important asset.

The other two sections present a DFT based mechanistic study of two distinct complexes. I expect that the proposed mechanisms will help to understand the underlying processes and will be of use when improving the current or designing novel catalysts. For example, the *in silico* modelling of such modified catalysts by simply changing the ligands in the structures of the developed mechanisms is a rather simple and cost-effective approach. Another possibility is to gain an even deeper understanding by identifying the intermediates proposed in the catalytic cycles experimentally as well, like we did during the work on the iridium based NHC complex.

VI. LIST OF PUBLICATIONS

Publications related to the dissertation

[1] **Fehér, P. P.**; Horváth, H.; Joó, F.; Purgel, M. DFT Study on the Mechanism of Hydrogen Storage Based on the Formate-Bicarbonate Equilibrium Catalyzed by an Ir-NHC Complex: An Elusive Intramolecular C–H Activation. *Inorganic Chemistry* **2018**, *57*, 5903–5914.

[2] **Fehér, P. P.**; Purgel, M.; Joó, F. Performance of Exchange–correlation Functionals on Describing Ground State Geometries and Excitations of Alizarin Red S: Effect of Complexation and Degree of Deprotonation. *Computational and Theoretical Chemistry* **2014**, *1045*, 113–122.

[3] **Fehér, P. P.**; Purgel, M.; Joó, F.; Calhorda, M. Phosphine containing noble metal complexes in catalytic hydrogenation reactions: A DFT study on the selectivity and viability of trans-dihydride pathways. *Organometallics*, under review

List of other publications

[1] Nagy, M.; Rácz, D.; Nagy, Z. L.; **Fehér, P. P.**; Kalmár, J.; Fábián, I.; Kiss, A.; Zsuga, M.; Kéki, S. Solvatochromic Isocyanonaphthalene Dyes as Ligands for silver(I) Complexes, Their Applicability in silver(I) Detection and Background Reduction in Biolabelling. *Sensors and Actuators B: Chemical* **2018**, *255*, 2555–2567.

[2] Nagy, M.; Rácz, D.; Nagy, Z. L.; Nagy, T.; **Fehér, P. P.**; Purgel, M.; Zsuga, M.; Kéki, S. An Acrylated Isocyanonaphthalene Based Solvatochromic Click Reagent: Optical and Biolabeling Properties and Quantum Chemical Modeling. *Dyes and Pigments* **2016**, *133*, 445–457.

[3] Nagy, M.; Rácz, D.; Kovács, S. L.; Lázár, L.; **Fehér, P. P.**; Purgel, M.; Zsuga, M.; Kéki, S. New Blue Light-Emitting Isocyanobiphenyl Based Fluorophores: Their Solvatochromic and Biolabeling Properties. *Journal of Photochemistry and Photobiology A: Chemistry* **2016**, *318*, 124–134.

[4] Józsa, É.; Purgel, M.; Bihari, M.; **Fehér, P. P.**; Sustyák, G.; Várnagy, B.; Kiss, V.; Ladó, E.; Ősz, K. Kinetic Studies of Hydroxyquinone Formation from Water Soluble Benzoquinones. *New Journal of Chemistry* **2014**, *38*, 588–597.

Presentations

[1] Fehér Péter Pál: Kvantumkémiai módszerek tesztelése a szulfonált alizarinvörös és palládium-komplexének izomereire, *XXXVII. Kémiai Előadói Napok*, Szeged, 2014, november 3-5.

[2] Fehér P.P., Purgel M.: A monoklóramin bomlása vizes közegben, *Szervetlen és Fémorganikus Kémiai Munkabizottság ülése*, Pécs, 2015. november 6-7.

[3] Purgel M., Fehér P.P.: M(III)EDTA komplexek intramolekuláris átrendeződései, *Szervetlen és Fémorganikus Kémiai Munkabizottság ülése*, Pécs, 2015. november 6-7.

[4] Péter Pál Fehér: Quantum chemical modeling of an acrylated isocyanonaphthalene based solvatochromic click reagent, *Graduate Conference on Theoretical Chemistry*; 1-3 September 2016, Keszthely, Hungary

[5] Fehér Péter Pál, Stirling András: A monoklóramin diszproporciójának modellezése, *KeMoMo–QSAR szimpózium*, Szeged, 2018. május 24-25.

Posters

[1] P. P. Fehér, M. Purgel and F. Joó: Performance of exchange-correlation functionals on describing ground state geometries and excitations of Alizarin Red S and its Palladium(II) complexes, *European Colloquium on Inorganic Reaction Mechanisms*, 17-20 June 2014, Debrecen, Hungary

[2] M. Purgel, P. P. Fehér; Hydro(Dehalo)genation Reactions by Semi- and Hydroquinones, *3rd CARISMA Meeting - Catalityc Routines for Small Molecule Activation*, Tarragona, 18-20 March 2015.

[3] P. P. Fehér, M. Purgel; A DFT study on the selectivity of phosphine and carbene containing noble metal complexes in hydrogenation reactions, *5th CARISMA Meeting - Catalityc Routines for Small Molecule Activation*, Lisszabon, Portugália, 2017. március 6-8.

[4] Péter Pál Fehér, Henrietta Horváth, Ferenc Joó and Mihály Purgel; DFT Study on the Mechanism of Hydrogen Storage Based on the Formate-Bicarbonate Equilibrium, *COST CHAOS Working Group Meeting*, Alcala, Spanyolország, 2018. március 22-23.

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List of publications related to the dissertation

Foreign language scientific articles in international journals (2)

1. **Fehér, P. P.**, Horváth, H., Joó, F., Purgel, M.: DFT Study on the Mechanism of Hydrogen Storage Based on the Formate-Bicarbonate Equilibrium Catalyzed by an Ir-NHC Complex: An Elusive Intramolecular C-H Activation.
   Inorg. Chem. 57 (10), 5903-5914, 2018. ISSN: 0020-1669.
   DOI: http://dx.doi.org/10.1021/acs.inorgchem.8b00382
   IF: 4.7 (2017)

2. **Fehér, P. P.**, Purgel, M., Joó, F.: Performance of exchange-correlation functionals on describing ground state geometries and excitations of Alizarin Red S: Effect of complexation and degree of deprotonation.
   Computational and Theoretical Chemistry. 1045, 113-122, 2014. ISSN: 2210-271X.
   DOI: http://dx.doi.org/10.1016/j.comptc.2014.06.025
   IF: 1.545

List of other publications

Foreign language scientific articles in international journals (4)

3. Nagy, M., Rácz, D., Nagy, Z. L., **Fehér, P. P.**, Kalmár, J., Fábián, I., Kiss, A., Zsuga, M., Kéki, S.: Solvatochromic isocyanonaphthalene dyes as ligands for silver(I) complexes, their applicability in silver(I) detection and background reduction in biolabelling.
   Sens. Actuator B. Chem. 255 (3), 2555-2567, 2018. ISSN: 0925-4005.
   DOI: http://dx.doi.org/10.1016/j.snb.2017.09.061
   IF: 5.667 (2017)

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4. Nagy, M., Rácz, D., Nagy, Z. L., Nagy, T., **Fehér, P. P.**, Purgel, M., Zsuga, M., Kéki, S.: An acrylated isocyanonaphthalene based solvatochromic click reagent: Optical and biolabeling properties and quantum chemical modeling.
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DOI: http://dx.doi.org/10.1016/j.dyepig.2016.06.036
IF: 3.473

5. Nagy, M., Rácz, D., Kovács, S. L., Lázár, L., **Fehér, P. P.**, Purgel, M., Zsuga, M., Kéki, S.: New blue light-emitting isocyanobiphenyl based fluorophores: Their solvatochromic and biolabeling properties.
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DOI: http://dx.doi.org/10.1016/j.jphotochem.2015.12.006
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6. Józsa, É., Purgel, M., Bihari, M., **Fehér, P. P.**, Sustyák, G., Várnagy, B., Kiss, V., Ladó, E., Ősz, K.: Kinetic studies of hydroxyquinone formation from water soluble benzoquinones.
New J. Chem. 38 (2), 588-597, 2014. ISSN: 1144-0546.
DOI: http://dx.doi.org/10.1039/c3nj01274c
IF: 3.086

Total IF of journals (all publications): 21,096
Total IF of journals (publications related to the dissertation): 6,245

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07 January, 2019

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