VNU Journal of Science: Natural Sciences and Technology

Original Article

Electronic Structures of Homodinuclear Platinum(II), Palladium(II) and Gold(I) Complexes Featuring Janus-type Benzoxazolin-2-ylidene Linkers

Nguyen Van Ha[*], Nguyen Thi Thu Hang

VNU University of Science, 19 Le Thanh Tong, Hanoi, Vietnam

Abstract: Electronic structures of a series of three homodinuclear platinum(II), palladium(II) and gold(I) complexes featuring Janus-type benzoxazolin-2-ylidene bridges and N,N-diisopropyl benzimidazolin-2-ylidene auxiliary ligands have been investigated. The gas-phase molecular structures of all compounds were first optimized using B3PW91 functional and SDD/6-31G(d) combination of basis sets. The nature of their frontier orbitals were then examined. The higher energy occupied molecular orbitals are predominantly d orbital of the metal in combination with π orbital of N,N-diisopropyl benzimidazolin-2-ylidene. On the other hand, the lower energy unoccupied molecular orbitals are π orbitals of the benzoxazolin-2-ylidene. TD-DFT calculations reveal that all the complexes require high energy ultraviolet photon for excitation and photoexcitations form excited state with decreased electron density on metal centers.

Keywords: Platinum(II), palladium(II), gold(I) complex, N-heterocyclic carbene, electronic structures, benzoxazolin-2-ylidene.

1. Introduction

N-hetero cyclic carbene (NHC) has attracted a great deals of attention in the past few decades due to their potential application in organic catalysis and organometallic chemistry [1-6]. The success of NHC can be attributed to their excellent turnability of steric and electronic properties owing to their very diverted structures [7,8]. The four common carbene backbones include imidazole, benzimidazole, triazole and imidazoline. Substitution of N-R group from such backbone, for example, imidazole and benzimidazole, an oxygen atom would lead to the formation of oxazolin-2-ylidene and benzoxazolin-2-ylidene, respectively (Figure 1).

It is clear from chemical intuition that oxazole and benzoxazole-derived carbenes are weaker donor NHC compared to the respective parents as N-R group is replaced by a more electron negative oxygen atom. However, the absence of substituent on the oxygen atom would also suggest N,O-heterocyclic carbenes

_____
[*] Corresponding author:
Email address: hanv@hus.edu.vn

exert a lesser steric hindrance toward the metal coordination sphere.
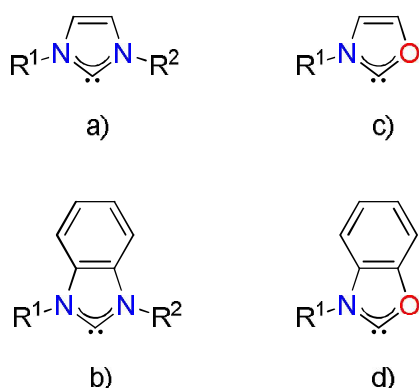

Figure 1. Generic structures of the N-heterocyclic carbenes derived from imidazole (a), benzimidazole (b), oxazole (c), and benzoxazole (d).

When R_1 substituent is simple hydrogen atom, transition metal complexes of this benzoxazolin-2-ylidene can be generated from 2- trimethylsiloxyphenyl isocyanide by an elegant two steps process, including (i) isocyanide coordination to a suitable metal center followed by (ii) cleavage of the oxygen-silicon bond. In case, a diisocyanide compound is used as starting material, the Janus-type N,O-heterocyclic carbene can be resulted (Scheme 1). [9,10]

Complexes of transition metals play essential roles in chemistry with potential application in various fields, such as metal-based drugs [11], catalysts [12] and photoactive compounds [13] for photocatalysts and luminescent materials. The design of metal complexes for the latter application often require a good understanding of electronic structures of the compounds.

Inspired by a current work on dinuclear gold(I) complex, and as part of our ongoing effort to investigate electronic structures of transition metal-N-heterocyclic carbenes and explore their potential application.

Scheme 1. Synthetic pathway to complexes featuring Janus-type benzoxazolin-2-ylidene (bozy) linkers
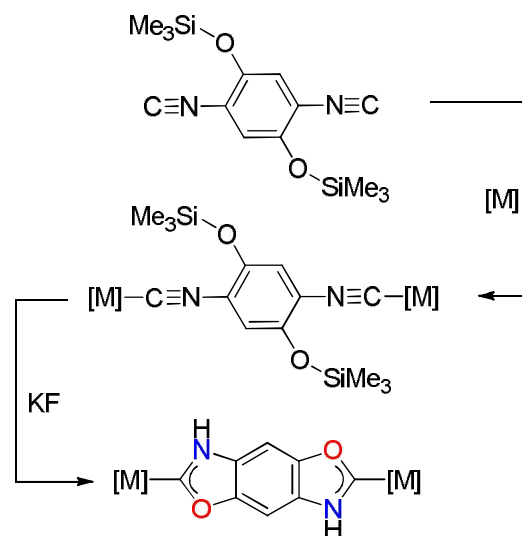
In this manuscript, we present our work on electronic structures of homodinuclear platinum(II), palladium(II) and gold(I) benzimidazolin-2-ylidene (bimy) complexes featuring Janus-type benzoxazolin-2-ylidene linkers. Structures of the compounds in this work is presented in Figure 2.

2. Methodology

All the complexes under studied were first optimized using Gaussian® 16 at B3PW91 level [14]. The 6-31G(d) basis set were employed for all the light atoms [15], whereas SDD basis set applied for Pt, Pd, Au and Br [16,17]. The nature of the stationary optimized points was confirmed to represent minima on energy potential surface by frequency analysis. Kohn-Sham orbitals were obtained directly from these calculations. TD-DFT calculations were carried out to calculate vertical excitation energy for all the complexes using optimized geometries at the same level of functional and basis set.
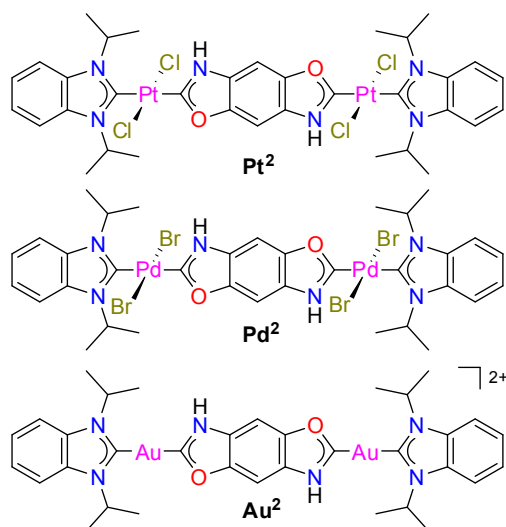
Figure 2. Structures of the compounds in this work

3. Results and Discussion

3.1. Geometry of the carbenes

Singlet-state gas-phased optimized geometries of Pt^2, Pd^2 and Au^2 are shown in Figure 3. Selected bond lengths and bond angles are listed in Table 1.
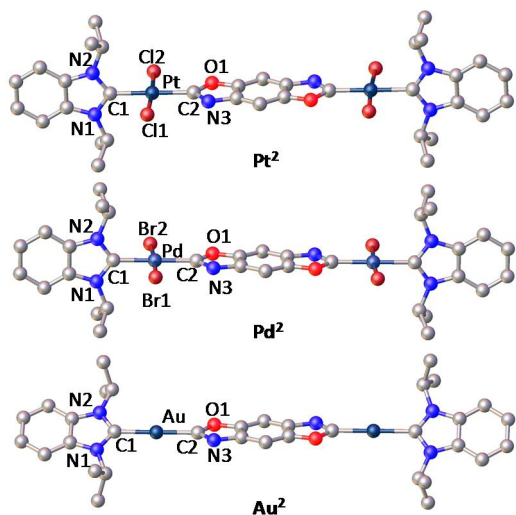

Figure 3. Optimized geometries for Pt^2, Pd^2 and Au^2

The optimized structures of the dinuclear complexes show highly symmetrical molecules. The platinum(II) center in Pt^2 and palladium(II) in Pd^2 complexes adapt square planar geometries, which a linear coordination is observed for the two gold(I) center in Au^2. The Pt–C, Pd–C and Au–C distances are closed to experimentally determined distance for reported complexes [10,18,19].

The metal carbene carbon (M–C1 and M–C2) distances slightly increase from Pd (2.021, 2.028 Å) to Pt (2.036, 2.009 Å) and Au (2.048, 2.026 Å). It is noted that, in Pt^2 and Au^2 structures, the M–C_{Bozy} bonds are longer than the respective M–C_{bimy} ones. On the other hand, Pd–C_{bimy} distance in Pd^2 is longer than its Pd–C_{bozy}. It is probably due the interaction between the N3 proton with the larger Br1 compared to Cl1 (Figure 4).

Table 1. Selected bond length (Å) and bond angle (°)

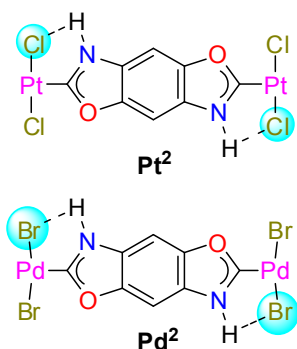| Parameters	Pt^2	Pd^2	Au^2
M–C1	2.036	2.021	2.048
M–C2	2.009	2.028	2.026
M–X1	2.550	2.532	-
M–X2	2.513	2.491	-
C1–N1	1.354	1.352	1.354
C1–N2	1.354	1.352	1.354
C2–N3	1.343	1.339	1.341
C2–O1	1.350	1.347	1.344
C1–M–C2	179.3	179.3	179.4
C1–M–X1	88.7	88.5	-
X1–M–X2	176.5	175.7	-
N1–C1–N2	107.5	107.8	107.8
O1–C2–N3	106.8	106.9	107.1

Figure 4. Interaction between proton in N–H and halide atoms.

Notably, while the benzoxazolin-2-ylidene (bozy) are coplanar with the coordination planes, the bimy carbenes in Pt^2 and Pd^2 are in exactly perpendicular, leading to orthogonal arrangement between bozy and bimy heterocycle. Such orientation would limit the delocalization of π conjugation system through out the entire molecules and the consequence will be discussed in the next session. On the other hand, alignment between bozy and two bimy planes are observed for Au^2 structures. The two bimy heterocycles are coplanar, and twisted from the bozy plane, forming dihedral angle of 35.2°.

3.2. Electronic structures of the compounds

Surface of frontier orbitals for the molecules are plotted in Figure 5 and their relative energy level are presented in Figure 6. For better description of molecular orbital, the Cartesian
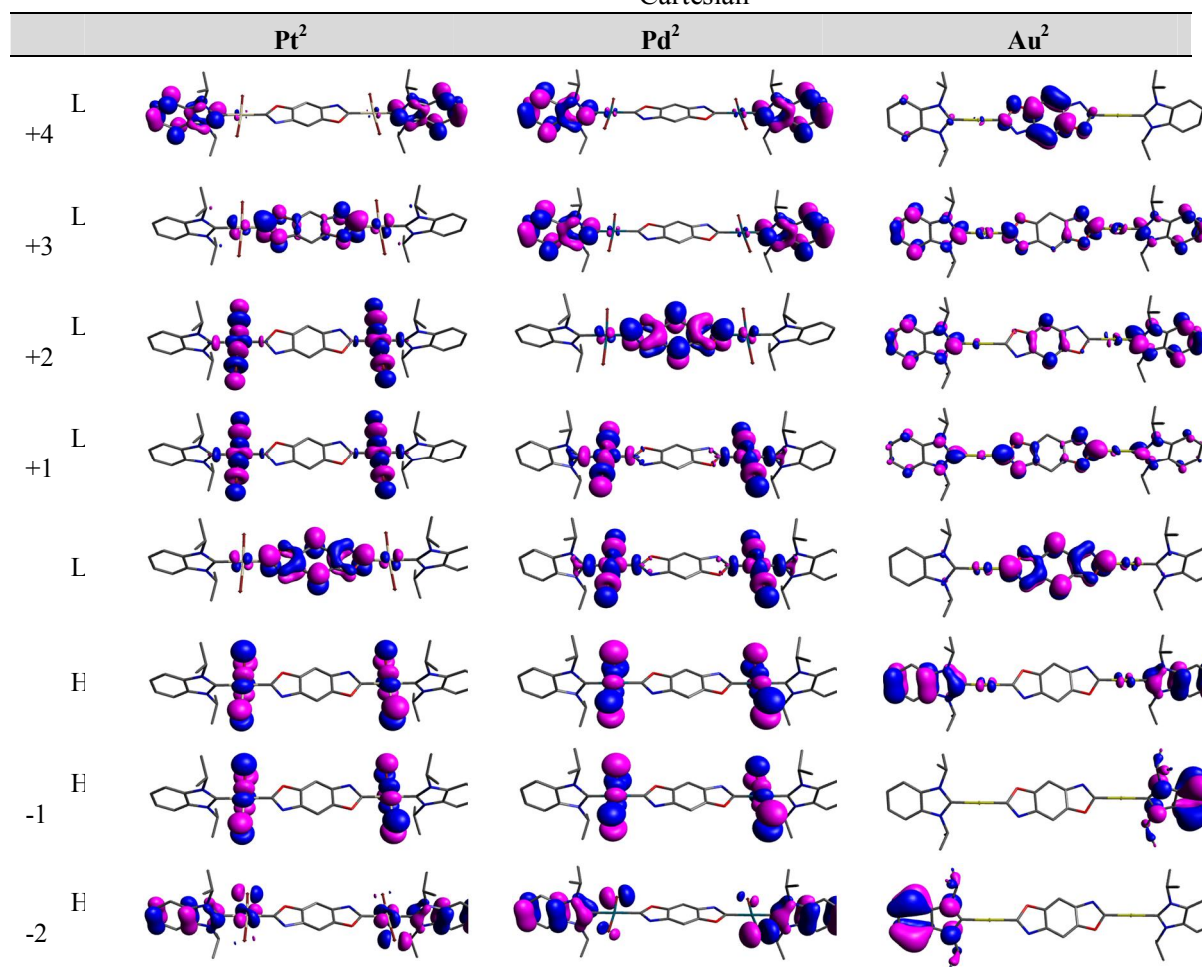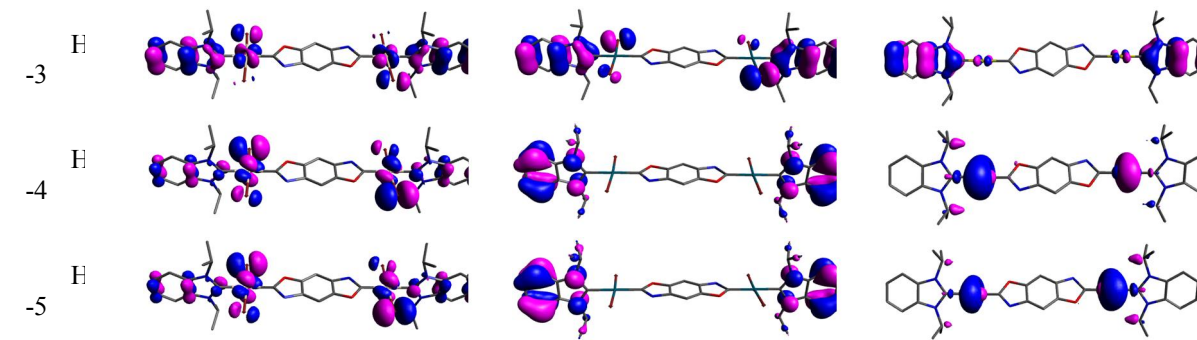
Figure 5. Frontier orbital surfaces of complex **Pt²**, **Pd²** and **Au²**.
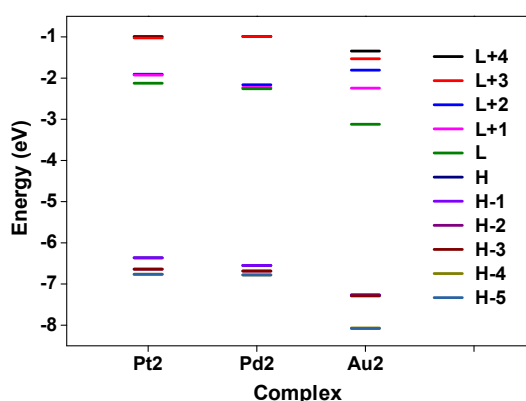

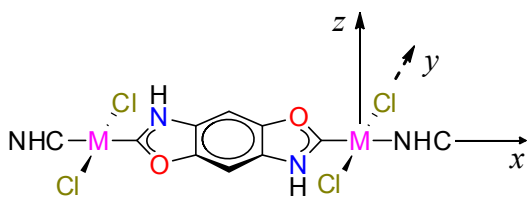Figure 6. Frontier orbital surfaces of complex Pt², Pd² and Au².

Figure 7. Definition of Cartesian coordinate.

coordinates are defined as presented in Figure 7. The frontier orbitals of Pt^2 and Pd^2 complexes are relatively similar in term of their nature and energy. the highest occupied molecular orbital (HOMO) and HOMO-1 orbitals for Pt^2 and Pd^2 are degenerate, and are basically combinations of metal d_{xz} orbital and the p_z orbitals of the halides.

The lower energy, HOMO-2 and HOMO-3 orbitals are largely π orbitals of the ^{i}Pr$_2$-bimy with small contribution from both platinum d_{xy} and the chloride p_x (in Pt^2) or bromide p_x (in Pd^2). The HOMO-4 and HOMO-5 of Pt^2 are p orbital of chloride and d orbital of platinum in principle. On the other hand, those orbitals in Pd^2 are predominantly delocalize on the pi orbital of bimy carbene. The d_{z^2} orbitals of platinum(II) and palladium(II) lie much lower in energy, and correspond to HOMO-8 with E = -6.80 eV (for Pt^2) and -6.96 eV (Pd^2). Lowest energy unoccupied molecular orbital (LUMO) for Pt^2 are π orbital of the bozy carbene. The LUMO+1 and LUMO+2 are basically combinations of $d_{x^2-y^2}$ of platinum(II) and p_y orbitals of chloride. On other hand, the LUMO and LUMO+1 for Pd^2 are $d_{x^2-y^2(Pd)} + p_{y(Br)}$ in nature. The LUMO+2 orbital is then the bozy π-orbital. The LUMO+3 for Pt^2 is localized on bozy fragment of the molecules, while its LUMO+4 are π orbital of bimy. In addition, both LUMO+3 and LUMO+4 for Pd^2 are π orbital of bimy. The nature of frontier orbitals in Au^2 quite differ from that of Pt^2 and Pd^2. All the HOMO, HOMO-1, HOMO-2, HOMO-3 orbitals are pi orbital of bimy in nature with negligible contribution from d orbital of gold(I). The LUMO and LUMO+4 are π orbital of bozy, while the LUMO+1, LUMO+2, LUMO+3 are delocalized over the entire molecules. In general, only in Au2, where the three carbene plane (bozy, bimy) are in near

coplanar that the π can delocalized over the entire molecules.

3.3. Vertical excitation energy of the molecules

To gain insight into interaction between complexes and light photon, TD-DFT calculation have been carried out. Results from the calculations, vertical excitation energy and oscillator strengths of the corresponding excitation are listed in Table 2.

Despite the presence of extended π conjugation system in the three complexes, the lowest energy excitations for all the three complexes are 358 nm (**Pt²**) and 330 nm (**Pd²** and **Au²**), indicating that the three compounds can only be excited using ultraviolet photons. This characters limit the application of such compounds as potential photocatalysts. Lowest

energy excitation of **Pt²** lead to a charge transfer from d_{Pt} to d_{Pt} and p_{Cl}, which is assignable to *d-d* transition and metal-to-ligand charge transfer (MLCT). Higher energy transitions correspond to charge transfer from *d* orbital of the platinum(II) center to the π system of the bozy moiety. Electronic transitions in **Pd²** and **Au²** appears to be more blue shifted, showing absorption centered at 330 and 300 nm for **Pd²** and **Au²**, respectively. Lowest energy excitation in **Pd²**, i.e 330 nm absorption, is assignable to the charge transfer from the *d* orbital of palladium(II) to π orbital of bozy or MLCT in nature. The transition of moderate intensity at 305 nm is also MLCT band, which promote electron from d_{z^2} orbital to π_{bozy} orbital. Much more intense transition is expected for *d-d* charge transfer for **Pd²** compound at 310 nm.

Table 2. Selected vertical transitions and assignment for **Pt²**, **Pd²** and **Au²**

Compound	Excitation energy (nm)	Oscillator strength	Transition	Contribution	Assignment
Pt²	358	0.005	H-8 → L+1	(40%)	$d_{Pt} \rightarrow d_{Pt} + p_{Cl}$
			H-9 → L+2	(39%)	$d_{Pt} \rightarrow d_{Pt} + p_{Cl}$
	346	0.011	H → L	(77%)	$d_{Pt} + p_{Cl} \rightarrow \pi_{bozy}$
	317	0.013	H-9 → L	(30%)	$d_{Pt} \rightarrow \pi_{bozy}$
			H-2 → L	(27%)	$\pi_{bimy} + d_{Pt} \rightarrow \pi_{bozy}$
			H-5 → L	(27%)	$p_{Cl} + d_{Pt} + \pi_{bimy} \rightarrow \pi_{bozy}$
	312	0.004	H-5 → L+2	(60%)	$p_{Cl} + d_{Pt} + \pi_{bimy} \rightarrow d_{Pt} + p_{Cl}$
	302	1.329	H-10 → L	(62%)	$d_{Pt} + \pi_{bozy} \rightarrow \pi_{bozy}$
Pd²	330	0.043	H → L+2	(67%)	$p_{Br} + d_{Pd} \rightarrow \pi_{bozy}$
	310	0.221	H-12 → L+1	(44%)	$p_{Br} + d_{Pd} \rightarrow d_{Pd} + p_{Br}$

			H-11 → L	(41%)	$p_{Br}+d_{Pd} \to d_{Pd}+p_{Br}$
	305	0.017	H-9 → L+2	(90%)	$d_{Pd} \to \pi_{bozy}$
Au²	330	0.623	H → L	(95%)	$\pi_{bimy} \to \pi_{bozy}$
	292	0.030	H-5 → L	(87%)	$d_{Au} \to \pi_{bozy}$

In the **Au²** complex, the only transition above 300 nm is HOMO → LUMO transition, which are basically inter ligand charge transfer LLCT. Population of π_{bozy} orbital by excitation from d orbital of gold(I) can also occur while using higher energy excitation (292 nm). In summary, most the excitations require ultraviolet photon and accompany with those photo excitation, decrease in the electron density from the Pt(II), Pd(II) and Au(I) metal centers are predicted.

4. Conclusion

Electronic structures of three homodinuclear complexes of platinum(II), palladium(II) and gold(I) complexes featuring Janus-type benzoxazolin-2-ylidene bridge and N,N-diisopropyl benzimidazolin-2-ylidene auxiliary ligands have been investigated. The results show that the benzoxazolin-2-ylidene linker are coplanar with coordination planes of Pt(II) and Pd(II) and are in perpendicular orientation with respect to the benzimidazolin-2-ylidene planes. In the gold(II) complexes, the three planes are in near coplanar. The frontier orbitals of the higher energy occupied molecular orbitals are predominantly d orbital of the metal in combination with π orbital of bimy carbene while the lower energy unoccupied molecular orbitals are π orbitals of the benzoxazolin-2-ylidene. TD-DFT calculations reveal that all the complexes require high energy ultraviolet photon for excitation in processes which lead to electron deficient metal centers.

Acknowledgments

References

[1] D. Bourissou, O. Guerret, F.P. Gabbaï, G. Bertrand, Stable Carbene, Chem. Rev. 100 (2000) 39-92. https://doi.org/10.1021/cr940472u.

[2] N. Marion, S.P. Nolan, Well-Defined N-Heterocyclic Carbenes−Palladium(II) Precatalyst for Cross-Coupling Reactions, Acc. Chem. Res. 41 (2008) 1440-1449. https://doi.org/10.1021/ar800020y.

[3] F.E. Hahn, M.C. Jahnke, Heterocyclic carbenes: synthesis and coordination chemistry, Angew. Chem., Int. Ed. 47 (2008) 3122-3172. http://doi.org/10.1002/anie.200703883.

[4] M.N. Hopkinson, C. Richter, M. Schedler, F. Glorius, An overview of N-heterocyclic carbenes, Nature 510 (2014) 485-496. https://doi.org/nature13384.

[5] W.A. Herrmann, N☐Heterocyclic Carbenes: A New Concept in Organometallic Catalysis, Angew. Chem., Int. Ed. 41 (2002) 1290-1309, https://doi.org/10.1002/1521-3773%282002 0415%2941%3A8%3C1290%3A%3AAID-ANIE1290%3E3.0.CO%3B2-Y.

[6] S. Díez-Gonzalez, N. Marion, S.P. Nolan, N-Heterocyclic Carbenes in Late Transition Metal Catalysis, Chem. Rev. 109 (2009) 3612-3676. https://doi.org/10.1021/cr900074m.

[7] L. Cavallo, A. Correa, C. Costabile, H.J. Jacobsen, Steric and electronic effects in the bonding of N-heterocyclic ligands to transition metals, Organomet. Chem. 690 (2005) 5407-5413. https://doi.org/10.1016/j.jorgan chem.2005.07.012.

[8] H. Clavier, S.P. Nolan, Percent buried volume for phosphine and N-heterocyclic carbeneligands: steric properties in organometallic chemistry, Chem. Commun. 46

(2010) 841-861. https://doi.org/10.1039/B92298 4A.

[9] W. P. Fehlhammer, U. Z. Plaia, Metallkomplexe funktioneller Isocyanide, XIII Bis(oxazolidin-2-yliden)-Komplexe von Mangan(I) und Nickel(II) / Metal Complexes of Functional Isocyanides, XIII Bis(oxazolidin-2-ylidene) Complexes of Manganese(I) and Nickel(II), Naturforsch., B: J. Chem. Sci. 41 (1986) 1005-1010. https://doi.org/10.1515/znb-1986-0813.

[10] M. Meier, T. T. Y. Tan, F. E. Hahn, H. V. Huynh, Donor Strength Determination of Benzoxazolin-2-ylidene, Benzobisoxazolin-2-ylidene, and Their Isocyanide Precursors by ^{13}C NMR Spectroscopy of Their Pd^{II} and Au^{I} Complexes. Organometallics, 36 (2017) 275-284. http://doi.org/ 10.1021/acs.organomet.6b00736.

[11] R. W. Y. Sun, A. L. F. Chow, X. H. Li, J. J. Yan, S. S. Y. Chui, C. M. Che, Luminescent cyclometalated platinum(II) complexes containing N-heterocyclic carbene ligands with potent in vitro and in vivo anti-cancer properties accumulate in cytoplasmic structures of cancer cells, Chem. Sci., 2 (2011) 728-736. http://doi.org/10.1039/c0sc00593b.

[12] A. Biffis, P. Centomo, A. D. Zotto, M. Zecca, Pd Metal Catalysts for Cross-Couplings and Related Reactions in the 21st Century: A Critical Review, Chem. Rev. 118 (2018) 2249-2295. http://doi.org/10.1021/acs.chemrev.7b00443.

[13] T. Strassner, Phosphorescent Platinum(II) Complexes with C^C* Cyclometalated NHC Ligands, Acc. Chem. Res. 49 (2016), 2680-1689. http://doi.org/ 10.1021/acs.accounts.6b00240.

[14] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C.

Fiolhais, Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation, Phys. Rev. B 46 (1992) 6671-6687. https://doi.org/10.1103/PhysRevB.46.6671.

[15] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, Self‐consistent molecular orbital methods. XX. A basis set for correlated wave functions, J. Chem. Phys. 72 (1980), 650-654. https://doi.org/10.1063/1.438955.

[16] D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß, Energy-adjustedab initio pseudopotentials for the second and third row transition elements: Molecular test for M2 (M=Ag, Au) and MH (M=Ru, Os). Theor. Chim. Acta, 78 (1991) 247-266. https://doi.org/10.1007/BF01112848.

[17] P. Schwerdtfeger, M. Dolg, W. H. Eugen Schwarz, A. B. Graham, P. D. W. Boyd. Relativistic effects in gold chemistry. I. Diatomic gold compounds. J. Chem. Phys. 91 (1989) 1762-1774. https://doi.org/10.1063/1.457082.

[18] M. Bouché, G. Dahm, A. Maisse-François, T. Achard, S. Bellemin-Laponnaz, Selective Formation of cis-N-Heterocyclic Carbene-PtII-Pnictogen Complexes and in vitro Evaluation of Their Cytotoxic Activities toward Cancer Cells, Eur. J. Inorg. Chem. (2016) 2828-2836. https://doi.org/ 10.1002/ejic.201600296.

[19] V. H. Nguyen, B. M. El Ali, H. V. Huynh, Stereoelectronic Flexibility of Ammonium-Functionalized Triazole-Derived Carbenes: Palladation and Catalytic Activities in Water, Organometallics, 37 (2018) 2358-2367. https://doi.org/10.1021/acs.organomet.8b00347.