1. Raziskovalna organizacija (*Research organisation)*:

Univerza v Ljubljani, Fakulteta za kemijo in kemijsko tehnologijo

2. Ime in priimek mentorja (*Name and surname of a mentor*):

Janez Košmrlj

3. Področje znanosti iz šifranta ARRS (*Primary research field*):

1.04.04

4. Kontaktni e-naslov mentorja (*Contact of a mentor)*:

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5. Kratek opis programa usposabljanja (*Short description of the program)*:

SLO

Več kot 90% industrijskih procesov za pripravo materialov, vsestransko uporabnih v vsakdanjem življenju, temelji na katalizi. Katalizator pospeši hitrost reakcije, kar poveča njeno selektivnost. To se posledično odraža v manjši količini stranskih produktov in s tem odpadkov. Za vzpostavitev trajnostne kemije in kemijske industrije je v zadnjem času ogromno truda vloženega v razvoj izboljšanih in naprednih katalitskih sistemov. V industrijski kemiji so učinkovite metode za tvorbe novih vezi ogljik–ogljik in ogljik–heteroatom neizmernega pomena. S paladijem katalizirane reakcije igrajo ključno vlogo pri sintezi številnih pomembnih spojin, kjer ima čedalje večji pomen homogena kataliza. Na tem pristopu temelji priprava zdravil (altiniklin), fungicidov (boskalid) in drugih pomembnih naravnih produktov (taksol, morfin), nekaterih tudi na večkilogramski skali. Na pomembnost teh reakcij opozarja Nobelova nagrada za kemijo Richardu Hecku, Ei-ichiju Negishiju in Akiri Suzukiju leta 2010. Na tej osnovi je bilo do sedaj razvitih veliko število reakcij pripajanja ("cross-coupling"), med njimi velja izpostaviti najbolj uporabljane – Suzukijevo, Heckovo, Hiyamovo, Negishijevo, Sonogashirovo, Stillejevo in Buchwald-Hartwigovo reakcijo. Navkljub široki uporabnosti s paladijem kataliziranih reakcij je pri industrijskih metodah in procesih dandanes potrebno upoštevati omejitve glede cene, kakor tudi zdravstvenih in okoljevarstvenih meril. Upoštevati je potrebno tudi omejene zaloge prehodnih kovin. Vse to trenutno uvršča optimizacijo učinkovitosti katalizatorjev in katalitskih procesov med ključne izzive v sintezni organski kemiji.

Tradicionalno se v homogeni katlizi uporabljajo fosfinski ligandi, ki pa imajo določene pomanjkljivosti. Iskanje alternativnih možnosti je vodilo do razvoja N-heterocikličnih karbenov (NHC), ki v mnogih primerih že presegajo učinkovitost fosfinov. Pred kratkim je razvoj na tem področju, kateremu je prispevalo tudi raziskovalno delo naše raziskovalne skupine (P1-0230), pripeljal do izjemno uporabnih NHC ligandov z mezoionsko 1,2,3-triazol-5-ilidensko (*tz*NHC) strukturo. Mi smo te ligande uporabili za pripravo paladijevih kompleksov, ki smo jih uporabili kot katalizatorje za tvorbo vezi C–C. Preliminarni rezultati so pokazali, da so ti katalizatorji boljši v primerjavi s prejšnjimi opisanimi katalizatorji za Sonogashirove reakcije. Topni so v vodi, so termično obstojni in učinkovito katalizirjo reakcije pripajanja arilbromidov s terminalnimi acetileni v prisotnosti zraka in v vodi kot topilu, brez dodatka aminov, bakra, fosfinov in kakršnihkoli drugih aditivov.

Navkljub dokazanemu potencialu v homogeni katalizi s kovinami prehoda, so *tz*NHC ligandi in njihovi kompleksi še zelo neraziskano področje in prostora za izboljšave je še veliko. Glavni cilj raziskovalnega dela mladega raziskovalca bo razvoj novih kompleksov kovin prehoda s Py-*tz*NHC ligandi, ki bodo predstavljali nadgradnjo obstoječih sistemov v trajnostni in visokoučinkoviti homogeni katalizi. Mladi raziskovalec bo študiral pripravo novih Pd(Py-*tz*NHC) kompleksov, nato pa preučeval njihove katalitske aktivnosti, predvsem pri Sonogashirovi, Heckovi, Suzuki-Miyaura in Buchwald-Hartwigovi reakciji. Posameznim reakcijam bo z eksperimentalnimi in teoretičnimi metodami študiral reakcijske mehanizme. Mladi raziskovalec se bo v času izpopolnjevanja naučil samostojnega planiranja eksperimentalnega dela, kritičnega razmišljanja in objektivnega ovrednotenja ter predstavitve znanstvenih rezultatov na znanstvenih konferencah in v obliki člankov v uglednih znanstvenih revijah.

ANG

Catalysis is used in over 90% industrial processes, facilitating the production of materials for various applications and products for everyday life. Catalysts increase the reaction rates and make the transformations more selective, thus leading to fewer by-products and less waste. To establish sustainable chemistry and chemical industry, substantial effort is devoted today to develop improved catalytic systems. The ability to form new carbon–carbon bonds, as well as carbon-heteroatom bonds, is of a tremendous importance in industrial chemistry. Palladium-catalysed reactions play a vital role in the production of many important chemicals, where homogeneous catalysis is rapidly growing. It has been used for the multi-kilogram scale preparation of many drugs (Altinicline), fungicides (Boscalid) as well as many other relevant compounds including natural products (Taxol, morphine), to name just a few. The impact of these reactions has been recognized by awarding the 2010 Nobel Prize in Chemistry to Richard Heck, Ei-ichi Negishi, and Akira Suzuki. A large number of cross-coupling variants have been developed to date including Suzuki, Heck, Hiyama, Negishi, Sonogashira, Stille, and Buchwald-Hartwig reaction.

In homogeneous catalysis, phosphines are traditionally employed as ligands for a transition metal. A quest for alternative entities has led to N-heterocyclic carbenes (NHCs), which have shown in many examples to exceed phosphines in their ability to bind to a variety of metals. Recently, also through the contributions of the research work from our research group (P1-0230), NHCs of a mesoionic 1,2,3-triazol-5-ylidene structure (*tz*NHCs) have emerged as a powerful subclass of these ligands. We used these ligands for the preparation of palladium complexes, which we applied as catalysts for the formation of C–C bond. Preliminary results have shown that these palladium complexes are superior to the previously reported catalysts for the Sonogashira reaction. They are water soluble and thermally stable, and efficiently catalyse the aryl bromides/terminal acetylene cross-coupling in air and in pure water, and in complete absence of amine, copper, phosphine and other additives.

Though *tz*NHCs exhibit high potential in homogeneous transition-metal catalysis, they are largely underdeveloped and the full catalytic power of their metal complexes is yet to be explored. The primary objective of the research work of young researcher will be to develop novel transition metal complexes of Py-*tz*NHC ligands that will be superior to the existing alternatives in sustainable and highly efficient homogeneous catalysis. Young researcher will study the preparation of new Pd(Py-*tz*NHC) complexes and will investigate their application for the Sonogashira, Heck, Suzuki-Miyaura, and Buchwald-Hartwig reactions. For each reaction the catalytic mechanism will be scrutinized experimentally, by using state of the art NMR and MS techniques and well as theoretically. Young researcher will acquire knowledge for critical evaluation and presentation of the results through scientific meetings and papers in established scientific journals.