Warsaw, 10/04/2021

Referee Report on PhD Thesis by Mr. Mehmet Mart

I had the pleasure of reading and assessing the *PhD Thesis* by Mr. Mehmet Mart (the Candidate), entitled "*DNA-supported palladium and its application in cross-coupling and carbonylation reactions*". This work has been conducted at the Faculty of Chemistry of the University of Wrocław, and supervised by Prof. D. Sc. Anna Maria Trzeciak.

For the convenience of the Candidate, my report is prepared in English, however the key, final formal statement is provided also in Polish language.

My general opinion about the Thesis is fully positive, and I am deeply convinced—for a number of reasons explained below—that based of these Thesis, Mr. Mehmet Mart should be accepted for the degree of *Doctor in Chemistry* from the University of Wrocław.

The *Thesis* are presented in a form of four publication reprints, the accompanying Supporting Information printouts, preceded with an introduction part presenting the background and state-of-the-art of the studied chemistry. The first part of the Thesis contains the title page, the abstract (Polish and English), table-of-contents (TOC), list of publications, acknowledgements etc. As required by law, the Thesis incorporate also photocopies of formal statements by other co-authors of Mr. Mart's publications, detailing their contribution to these papers. This part spans on 44 pages, followed by printouts of the papers and their supplementary information (SI) parts. The copy of the Thesis sent to me was printed in a form of a A4-size book, with a mustard-coloured cardboard cover.

The general introductions provided in the first part of the thesis presents the obtained scientific results from a personal perspective, and is—in general—easy to follow, instructive, and prepared in a highly scholarly manner.

This Introduction consists of the following major parts: Introduction to palladium catalysed cross couplings and carbonylation in general; Overview of Pd-nanoparticles (PdNPs) use in these coupling reactions, and—specifically—PdNPs immobilised on DNA (ca. 10 pages). Next the Candidate described his resulsts, starting from definition of the "Aims of the Thesis" and then describing the research conducted (ca. 20 pages). These results are described briefly, but in good detail, and in general make a good story. Importtantly, this "personal" part of the *Thesis* is well-written; containing practically no

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major language misspellings and no grammatical nor stylistic mistakes. References are correctly organised and are comprehensive. Schemes are informative and easy to read. (In my copy of the *Thesis*, the schemes were printed in bold letters and the lines are too thick—although fully readable). It shall be noted that a number of artwork, especially graphs (e.g. TEM pictures) and charts (e.g. particle distribution) are directly reproduced (or very similar to those) from the original publications. This is well understandable, of course. This "personal" part ends with "Conclusions" and "References". So, it is truly a regular thesis in a miniature. Conclusion part (1¼ page) is concise, but well written, and informative enough. In general, the first part of the Thesis is just of right size, and makes reading of the original papers an easier task.

Next goes the original papers, and the Referee briefly describe them one-by-one, in the same order as they are in the Thesis.

The first paper is published in an open-access journal *Catalysts* and entitled "*Pd/DNA as Highly Active and Recyclable Catalyst of Suzuki–Miyaura Coupling*" (*Catalysts* **2018**, *8*, 552; doi:10.3390/catal8110552). As clearly stated in the title, this work targets the Pd/DNA system prepared by mixing simple palladium precursors, such as $Pd(OAc)_2$ or $PdCl_2$, with salmon fish sperm DNA. Such prepared Pd(II)/Pd(0) catalyst was found by the Candidate to efficiently catalyse the Suzuki–Miyaura cross-coupling between various model aryl bromides and phenylboronic acids. Importantly, the catalyst can be easily recovered by simple phase separation and then reused in seven consecutive cycles, keeping the high activity.

In the context of this paper, I would like again state that adding in the Thesis the rather detailed Introduction and state-of-the-art part was a very good decision, because in the source publication the introduction part was kept minimal.

The second paper is published in Elsevier's *Molecular Catalysis* journal (*Molecular Catalysis* **2019**, *462*, 28–36; doi:10.1016/j.mcat.2018.10.013) with the title "*Pd/DNA as a highly active and recyclable catalyst for aminocarbonylation and hydroxycarbonylation in water: The effect of $Mo(CO)_6$ on the reaction course*". Again, the title tells almost all: A Pd/DNA catalyst was prepared similarly as before, using the salmon fish sperm DNA. The analysis shows that the catalyst is composed of ca 20% of Pd(0) nanoparticles and of Pd(II)/DNA complex (the later was *en route* reduced to catalytically active Pd(0) as evidenced by XPS). This system was tested in the aminocarbonylation of iodobenzene with different amines in water under 1 atm of CO and with $Mo(CO)_6$ as the source of CO. The latter showed sometimes better selectivity than gaseous CO. Again, the catalyst can be recovered and reused (this time in four subsequent runs) with high activity.

The third paper, "*Solvent switchable Pd/DNA catalyst in carbonylative Sonogashira coupling*" is published in the same journal (*Molecular Catalysis* **2020**, *494*, 111124; doi:10.1016/j.mcat.2020.111124). In this work, Pd/DNA was applied in the carbonylative Sonogashira coupling (using gaseous CO at 1 atm pressure) when DMF was used as a solvent. In the presence of water, however, the selectivity was changed towards tolanes (diarylalkynes) formation, via standard (not carbonylative) Sonogashira reaction. Mr. Mart checked that this process is catalysed by both soluble palladium species in addition to Pd/DNA. The effect of water was explained by the Authors by the competition of water molecules with CO as the ligands for palladium, thus suppressing the effective CO activation.

The last paper, that just very recently appeared in press (*Molecular Catalysis* **2021**, *502*, 111365; doi: 10.1016/j.mcat.2020.111365) deals with Pd/DNA-catalysed synthesis of β-enaminones using trialkylamines. The title transformation consists of the interesting cascade of carbonylative Sonogashira coupling of aryl iodides with terminal alkynes and the oxidative dealkylation of tertiary amines leading to β-enaminones. (Mr. Mart—together with his Supervisor?—proposed a convincing reaction mechanism of this transformation). As previously, the fish sperm-immobilised PdNPs were successfully recovered and used in several subsequent reactions.

To each publication reprint, printouts of the complete Supporting Information have been attached. The experimental parts are of course the most important and interesting, as they can tell about the Candidate's skills and technique. I was not surprised by the general very high quality of the corresponding experimental parts, in which the preparation of the catalysts, and the analytical data of the products etc, were described in details. The attached SI parts demonstrate not only the technical quality but also the significant amount of work invested by the Candidate during execution of his Thesis. After reading the experimental procedures reproduced in the Thesis, I am fully convinced that all the results reported there can be easily repeated and reproduced, as the descriptions are of high quality and I was unable to find any major mistakes. (it is required in SI, but anyway *bravo* for a number of NMR spectra reproduced as the pictures!).

The original scientific goal of this PhD work was to obtain and to characterise Pd(II)→Pd(0) fish DNA systems and to test them in C–C bond forming reactions, including Sonogashira and Suzuki–Miyaura couplings, and also in the more challenging carbonylative versions of the above. *This goal has been fully achieved*.

From my perspective, as a humble practitioner in catalysis, I judge Mr. Mart's results very interesting. The syntheses of the Pd/fish sperm DNA catalysts seems operationally simple, but these systems are not simple as far as their composition and the nature of palladium concerns. The Candidate's whole work in characterising and testing of these recyclable cat-

alysts is of high quality. This way, the obtained results are not only interesting from the theoretical point of view, but also have potential practical importance.

Importantly, all of the results discussed in the *Thesis* are already published in a specialised journals of international renown, such as *Molecular Catalysis*. This means that not only the Undersigned checked the quality of this work, but it was firstly positively appraised by the set of international experts—the reviewers for the journals. These papers are co-authored by Prof. Trzeciak (the Supervisor) and sometimes by Prof. Tylus (XPS measurements), and I wish to stress that in the each case Mr. Mart is *the first author*, and there are no other PhD students co-authoring his papers.

To sum up, I can state that despite the field of activity the Candidate had chosen is very ambitious, he was fully able to manage the task. The *Thesis* as a whole is a substantial and original contribution to knowledge of the subject of organometallic chemistry in general, and to Pd-catalysis in specific. Therefore, I am fully confident that Mr. Mehmet Mart shall obtain the *Doctor in Chemistry* title. Thus, I recommend without any hesitation his *Thesis* to be accepted in University of Wrocław for a Ph.D. Degree.

Po zapoznaniu się z niniejszą Rozprawą nie mam żadnych wątpliwości, że wszystkie wymogi Ustawy są spełnione, a sama praca napisana jest bardzo dobrze i świadczy o dobrym przygotowaniu teoretycznym i praktycznym Doktoranta. W związku z tym wnioskuję o przyjęcie rozprawy doktorskiej Pana Mehmeta Marta, oraz o dopuszczenie jej do dalszych etapów przewodu doktorskiego.

sincerely,

Prof. Dr. habil. Karol Grela