

UNIVERSITI TEKNOLOGI MARA

**SYNTHESIS AND
CHARACTERIZATION OF
PALLADIUM(II) AND NICKEL(II)
COMPLEXES OF SCHIFF BASES
AND THE POTENTIAL OF THE
PALLADIUM(II) COMPLEXES AS
CATALYSTS FOR
C-C BOND FORMATION**

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Thesis submitted in fulfillment
of the requirements for the degree of
Doctor of Philosophy


Faculty of Applied Sciences

August 2014

AUTHOR'S DECLARATION

I declare that the work in this thesis/dissertation was carried out in accordance with the regulations of Universiti Teknologi MARA. It is original and is the result of my own work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted to any other academic institution or non-academic institution for any degree qualification.

I, hereby, acknowledge that I have been supplied with the Academic Rules and Regulations for Post Graduate, Universiti Teknologi MARA, regulating the conduct of my study and research.

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ABSTRACT

This study reports the synthesis, characterization and catalytic activities of palladium(II) Schiff base complexes, both as homogeneous and MCM-41 supported heterogeneous catalysts for cross-coupling C-C bond formation reactions. Three broad groups of inexpensive Schiff base ligands (L1, L2 and L3) have been synthesized through condensation process between four benzylamine derivatives with aldehyde or ketone in 1:1 molar ratio. 12 ligands and 20 metal complexes of Pd(II) and Ni(II) have been successfully obtained. The metal complexes were prepared through the complexation reaction between the Schiff base ligands with Pd(II) and Ni(II) acetates in a 2:1 molar ratio. All the synthesized ligands and complexes have been characterized using CHN elemental analysis, infrared, ^1H and ^{13}C NMR, UV-Visible, melting point determination, molar conductance and magnetic susceptibility. The molecular geometries of ten complexes namely PdL1c, PdL1d, NiL1c, NiL1d, PdL2a, PdL2d, PdL3b, PdL3c, PdL3d and NiL3d have been solved by single crystal X-ray crystallography. It revealed that these Schiff bases behave as bidentate ligands, coordinating through the imine N and phenolic O donor atoms, as also shown by the infrared data. Magnetic susceptibility suggests square planar Pd(II) and Ni(II) complexes, while non-electrolytic behaviour indicated the absence of ions in chloroform. PdL3a, PdL3b, PdL3c and PdL3d have been chosen to catalyze the Heck and Suzuki cross-coupling reactions because of their good performances in the screening phase. Three parameters have been chosen for optimization of the reaction conditions, which were types of bases, catalyst loadings and reaction temperatures. This study has found that the complexes performed well at a relatively low catalyst loading of 1 mmol%. They were effective catalysts for Heck reaction of iodobenzene with methyl acrylate to form methyl cinnamate and for Suzuki reaction of iodobenzene with phenylboronic acid to form 1,1'-biphenyl where the conversions of iodobenzene reached up to 100% at 100°C within 24 hours of reaction time. For the heterogeneous catalytic investigations, two modified MCM-41 moieties, namely MCM-41-Pd-Ovan and MCM-41-PdL3c, were investigated. The PdL3c complex was chosen for heterogeneous catalytic study due to its superior performance during homogeneous catalysis study. The synthesized MCM-41 supported species were characterized using CHN elemental analysis, ICP-OES, infrared, XRD, TGA-DTA, BET and nitrogen sorption and FESEM-EDX analyses. ICP-OES data revealed that the palladium loading in MCM-41-Pd-Ovan and MCM-41-PdL3c were 0.259 and 0.097 mmol g⁻¹, respectively. Both were found to be moderately good catalysts. Some leaching of active species in reaction mixtures especially for the MCM-41-Pd-Ovan was detected. The leaching was found to be less extensive for the MCM-41-PdL3c. As additional work in this study, six metal complexes namely PdL1c, PdL1d, PdL3d, NiL1c, NiL1d and NiL3d have undergone antibacterial investigation as a representatives group. The complexes have shown a little or no inhibition against *E. coli*, *B. subtilis* and *S. aureus*, most likely due to the low solubility of the complexes in DMSO solvent.

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