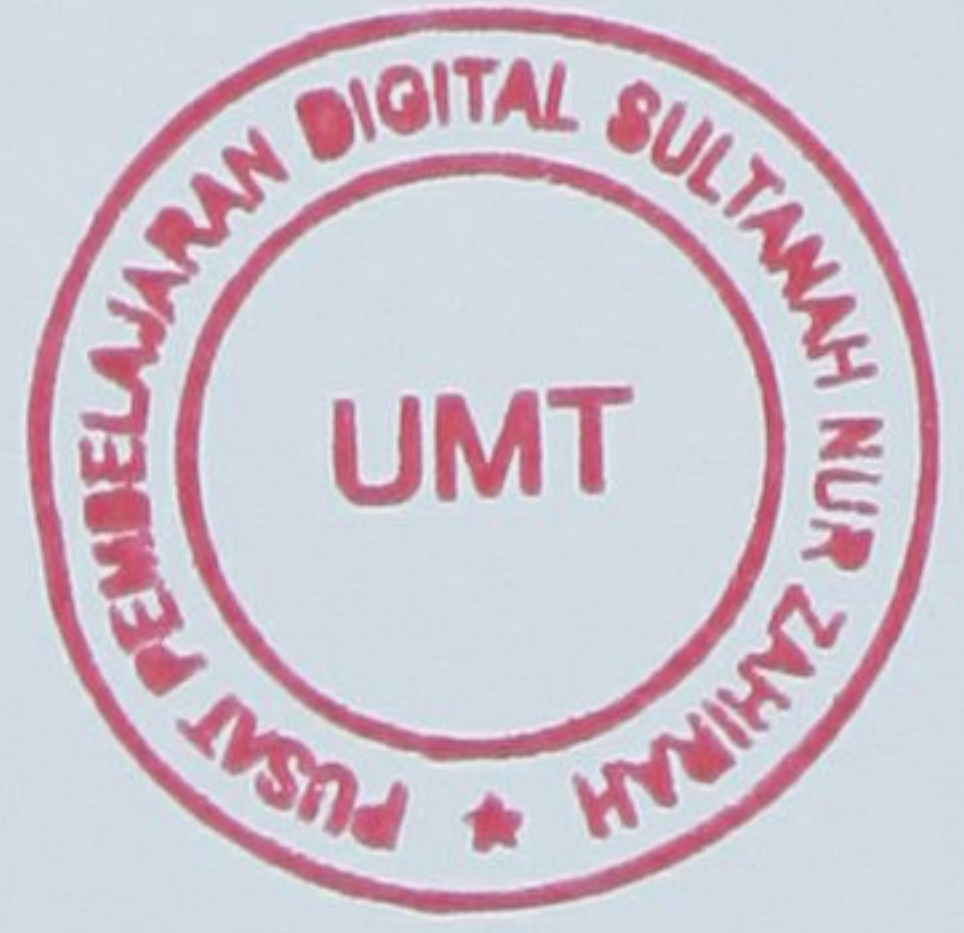


CATALYTIC MIZOROKI-HECK REACTIONS OVER PALLADIUM(II)
SCHIFF BASE COMPLEXES IN HOMOGENEOUS AND
HETEROGENEOUS POLYANILINE SUPPORTED SYSTEMS

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Catalytic mizoroki-heck reactions over palladium(II) schiff base complexes in homogeneous and heterogeneous polyaniline supported systems / Siti Kamilah Che Soh.

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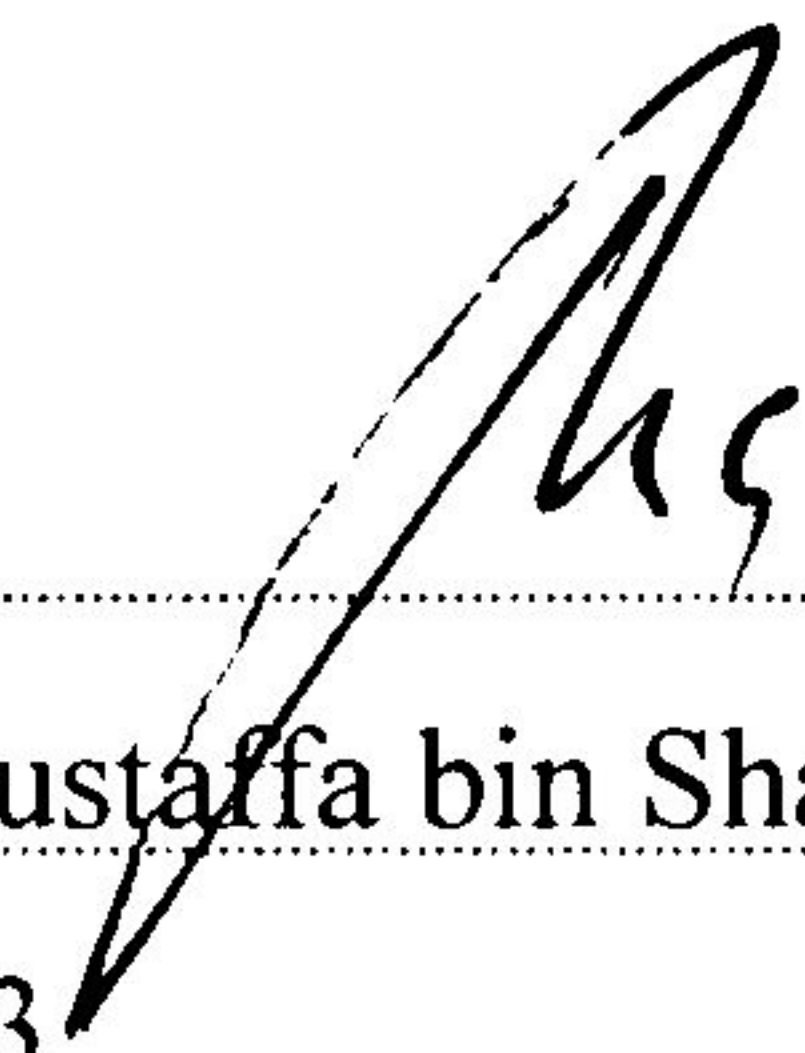

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CATALYTIC MIZOROKI-HECK REACTIONS OVER PALLADIUM(II) SCHIFF
BASE COMPLEXES IN HOMOGENEOUS AND HETEROGENEOUS
POLYANILINE SUPPORTED SYSTEMS

SITI KAMILAH BINTI CHE SOH

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy (Chemistry)

Faculty of Science
Universiti Teknologi Malaysia

APRIL 2013

I declare that this thesis entitled "*Catalytic Mizoroki-Heck Reactions over Palladium(II) Schiff Base Complexes in Homogeneous and Heterogeneous Polyaniline Supported Systems*" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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To my beloved family.....

Dzuhir Mohamad & Muhammad Dinie Karomi

thank you for waiting all this while

and to someone special...

Hjh. Ronidah Hj. Hussain

thank you for everything

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ABSTRACT

The palladium catalysed Mizoroki-Heck reactions represent one of the most effective methods for the formation of carbon-carbon bonds in organic synthesis. This research reports on the synthesis, characterization and catalytic activity of homogenous and polyaniline (PANI) supported palladium(II) Schiff base complexes. Two series of seven symmetrical N_2O_2 -Schiff base ligands, $C_{21}H_{26}N_2O_2$ (**3.3**), $C_{19}H_{22}N_2O_2$ (**3.5**), $C_{33}H_{50}N_2O_2$ (**3.7**), $C_{19}H_{22}N_2O_4$ (**3.9**), $C_{21}H_{26}N_2O_2$ (**3.15**), $C_{35}H_{54}N_2O_2$ (**3.16**) and $C_{21}H_{26}N_2O_4$ (**3.17**) have been prepared through condensation reaction between primary amines 1,3-diaminopropane (**3.2**) or 2,2-dimethyl-1,3-propanediamine (**3.14**) with the appropriate aldehyde or ketone compounds in the molar ratio 1:2. The corresponding palladium(II) Schiff base complexes were successfully synthesized through the complexation reaction between the Schiff base ligands with palladium(II) acetate in a 1:1 molar ratio. All products were characterized by elemental CHN analysis, FTIR and NMR spectroscopic techniques. The spectroscopic data suggested that the ligands acted as N_2O_2 -tetradentate, coordinating to the Pd atom through both the azomethine N atoms and phenolic O atoms. The structure of ligands (**3.3**) and (**3.16**) and Pd complexes $C_{19}H_{20}N_2O_2Pd$ (**3.11**), $C_{35}H_{52}N_2O_2Pd$ (**3.19**) and $C_{21}H_{24}N_2O_4Pd$ (**3.20**) were also elucidated by single crystal X-ray crystallographic analysis. The X-ray crystallographic analytical data confirmed the N_2O_2 -tetradentate characteristic and showed that the palladium complexes adopted a square planar geometry. The synthesized palladium(II) Schiff base complexes were subjected to the homogeneous catalytic Mizoroki-Heck reaction of 4-bromoacetophenone (**3.21**) with methyl acrylate (**3.22**). Complexes (**3.12**) and (**3.19**) gave conversion of (**3.21**) up to 100% using sodium acetate (NaOAc) as a base at temperature 120-140 °C after 6 and 12 hours of reaction. Both complexes were then separately immobilized onto PANI to give two new heterogeneous catalysts. The PANI supported catalysts (PANI-[**3.12**] and PANI-[**3.19**]) were characterized by several techniques such as AAS, FTIR, XRD, TG-DTA, BET surface area and FESEM-EDX analyses. AAS elemental analytical data revealed that the amount of palladium loading is 0.1012 mmol g⁻¹ and 0.3653 mmol g⁻¹ for PANI-[**3.12**] and PANI-[**3.19**], respectively. The catalytic performance of PANI-[**3.12**] and PANI-[**3.19**] were also evaluated in the Mizoroki-Heck reaction between (**3.21**) with (**3.22**). Both catalysts gave 100% conversion of (**3.21**) with turnover number equals to 100 mmol product/mmol Pd after 24 and 48 hours when NaOAc was used as a base and *N,N*-dimethylacetamide (DMA) as a solvent. The supported catalyst could be reused at least four times without noticeable decrease in the conversion when water-DMA mixed solvents is used in the reaction.

ABSTRAK

Tindak balas Mizoroki-Heck yang bermungkinan paladium merupakan salah satu kaedah paling efektif bagi pembentukan ikatan karbon-karbon dalam sintesis organik. Penyelidikan ini melaporkan mengenai sintesis, pencirian dan aktiviti pemangkinan bagi kompleks bes Schiff paladium(II) homogen dan berpenyokong polianilina (PANI). Dua siri yang terdiri daripada tujuh ligan bes Schiff- N_2O_2 bersimetri iaitu $C_{21}H_{26}N_2O_2$ (3.3), $C_{19}H_{22}N_2O_2$ (3.5), $C_{33}H_{50}N_2O_2$ (3.7), $C_{19}H_{22}N_2O_4$ (3.9), $C_{21}H_{26}N_2O_2$ (3.15), $C_{35}H_{54}N_2O_2$ (3.16) dan $C_{21}H_{26}N_2O_4$ (3.17) telah disediakan melalui tindak balas kondensasi antara amina primer 1,3-diaminopropana (3.2) atau 2,2-dimetil-1,3-propanadiamina (3.14) dengan sebatian keton atau aldehid yang bersesuaian dalam nisbah mol 1:2. Kompleks bes Schiff paladium(II) yang sepadan juga telah berjaya disintesis melalui tindak balas pengkompleksan antara ligan bes Schiff dengan paladium(II) asetat dalam nisbah mol 1:1. Semua hasil telah dicirikan menggunakan analisis unsur CHN, spektroskopi FTIR dan NMR. Data spektroskopi menunjukkan bahawa semua ligan bertindak sebagai tetradentat- N_2O_2 , terkoordinat kepada atom Pd melalui kedua-dua atom N azometin dan atom O fenolik. Struktur ligan (3.3) dan (3.16) serta kompleks paladium $C_{19}H_{20}N_2O_2Pd$ (3.11), $C_{35}H_{52}N_2O_2Pd$ (3.19) dan $C_{21}H_{24}N_2O_4Pd$ (3.20) juga telah ditentukan menggunakan analisis kristalografi sinar-X hablur tunggal. Data analisis kristalografi sinar-X mengesahkan ciri tetradentat- N_2O_2 dan kompleks paladium memiliki geometri segi empat sama sesatah. Kompleks bes Schiff paladium(II) yang terhasil telah diuji sebagai mangkin homogen dalam tindak balas Mizoroki-Heck antara 4-bromoasetofenon (3.21) dengan metil akrilat (3.22). Kedua-dua kompleks (3.12) dan (3.19) memberikan penukaran (3.21) sehingga 100% apabila menggunakan natrium asetat (NaOAc) sebagai bes pada suhu 120-140 °C setelah 6 dan 12 jam masa tindak balas. Kedua-dua kompleks ini secara berasingan dipegunkan ke atas PANI bagi menghasilkan dua mangkin heterogen yang baru. Mangkin berpenyokong (PANI-[3.12] dan PANI-[3.19]) dicirikan melalui beberapa teknik misalnya AAS, FTIR, analisis XRD, TG-DTA, luas permukaan BET dan FESEM-EDX. Data analisis unsur AAS menunjukkan jumlah muatan paladium masing-masing adalah 0.1012 mmol g^{-1} dan 0.3653 mmol g^{-1} bagi PANI-[3.12] dan PANI-[3.19]. Prestasi PANI-[3.12] dan PANI-[3.19] sebagai mangkin juga diuji dalam tindak balas Mizoroki-Heck antara (3.21) dan (3.22). Kedua-dua mangkin memberikan penukaran (3.21) sehingga 100% dengan nombor perolehan yang bersamaan dengan 100 mmol produk/mmol Pd selepas 24 dan 48 jam masa tindak balas apabila NaOAc digunakan sebagai bes dan *N,N*-dimetilasetamida (DMA) sebagai pelarut. Mangkin berpenyokong ini boleh diguna semula sekurang-kurangnya sebanyak empat kali tanpa pengurangan penukaran yang ketara apabila pelarut bercampur air-DMA digunakan dalam tindak balas.