SYNTHESIS AND CHARACTERISATION OF SOME THIOUREA-THIAZOLE COMPLEXES AS HOMOGENEOUS CATALYSTS IN HECK CROSS-COUPLING REACTION

SITI AISHAH BINTI ZAKARIA

MASTER OF SCIENCE
UNIVERSITI MALAYSIA TERENGGANU
MALAYSIA

2011

SYNTHESIS AND CHARACTERISATION OF SOME THIOUREA-THIAZOLE COMPLEXES AS HOMOGENEOUS CATALYSTS IN HECK CROSS-COUPLING REACTION

SITI AISHAH BINTI ZAKARIA

MASTER OF SCIENCE

UNIVERSITI MALAYSIA TERENGGANU

MALAYSIA

2011

SYNTHESIS AND CHARACTERISATION OF SOME THIOUREA-THIAZOLE COMPLEXES AS HOMOGENEOUS CATALYSTS IN HECK CROSS-COUPLING REACTION

SITI AISHAH BINTI ZAKARIA

Thesis Submitted in Fulfillment of the Requirement for the Degree of Master of Science in the Faculty of Science and Technology
Universiti Malaysia Terengganu

September 2011

Abstract of thesis presented to the Senate of Universiti Malaysia Terengganu in fulfillment of the requirement for the degree of Master of Science

SYNTHESIS AND CHARACTERISATION OF SOME THIOUREA-THIAZOLE COMPLEXES AS HOMOGENEOUS CATALYSTS IN HECK CROSS-COUPLING REACTION

SITI AISHAH BINTI ZAKARIA

September 2011

Chairperson : Mohd Sukeri Mohd Yusof, Ph.D.

Member : Wan Mohd Khairul Wan Mohamed Zin, Ph.D.

Faculty : Science and Technology

Thiourea derivatives are interesting compounds and can be designated by adding the substituent group on the both terminal nitrogen atoms. This feature endows this derivative with multifunctional coordination ability with metal and the complexes have been applied in numerous fields. In this study, the complexation of Pd(II) with thiourea-thiazole ligands were carried out in order to investigate their catalytic behaviour in Heck Cross-coupling reaction as catalyst. The reactions between aryl carbonyl isothiocyanate with 2-aminobenzothiazole have resulted the mixtures of two compounds namely thiourea-thiazole and thiazole. However, when alkyl carbonyl isothiocyanate reacted with 2-aminobenzothiazole, thiazole compounds have formed in the reaction. Therefore, the ligands of six thiourea-thiazole compound (**TH1-TH3**, **TH8-TH10**) and ten thiazole compound (**TD1-TD10**) have been successfully synthesised. The complexation of four selected synthesised ligands with Pd(II) (**PdTH1**, **PdTH2**, **PdTH3**) and Hg(II) (**HgTD6**) have been successfully designated. All synthesised compounds were characterised by typical spectroscopic and analytical methods namely Fourier Transform Infrared (FTIR), ^{1}H and ^{13}C Nuclear Magnetic Resonance (^{1}H and ^{13}C NMR), microelemental analyses (CHNS) and the determination of melting point. Whilst, the molecular structures of five synthesised ligands (**TH2**, **TH10**, **TD1**, **TD8** and **TD10**) and a complex of **HgTD6** were confirmed by using single crystal X-ray diffraction analyses. The FTIR spectra of the ligands show the band of interest which are ν(N-H), ν(C=O), ν(C=N) and ν(C-N) at around 3300 cm^{-1}, 1600 cm^{-1}, 1500 cm^{-1} and 1400 cm^{-1} respectively. Meanwhile, the bands at around 700 cm^{-1} are assigned for stretching ν(C=S) of thiourea-thiazole compounds. In ^{1}H NMR spectra, the formation of thiourea moiety in thiourea-thiazole compounds are proven based on the appearance of two NH

signals at δ_H 12.18-12.66 ppm (–N**H**C=O) and δ_H 13.95-14.28 (–N**H**C=S). While, for thiazole compounds, single NH signal appears at δ_H 12.03-12.72 ppm (–N**H**C=O). Whilst, in ^{13}C NMR spectra for thiourea-thiazole compounds the signals of carbon carbonyl and carbon thione are appeared at δ_C 166.19-170.56 ppm and δ_C 177.71-182.11 ppm, respectively. Whereas, the carbon carbonyl signal for thiazole compounds can be observed at around δ_C 150 ppm. The X-ray diffraction analyses of ligands **TH2** and **TH10** reveal that both of the compounds adopt *cis-trans* configuration with respect to the position of the benzothiazole and benzoyl groups relative to the thiono S atom, across their C-N bonds. On the other hand, the FTIR spectra of **PdTH1**, **PdTH2** and **PdTH3** complexes show significant shift in their frequencies with ν_Δ 3-115 cm^{-1} compared to the ligands. While the FTIR complex of **HgTD6** and its ligand (**TD6**) show no significant changes in their spectra. The coordination of Pd(II) metal towards ligands are suggested from the most shifted signals in ^{13}C NMR. Thus, the complexes of **PdTH1** and **PdTH3** are proposed to coordinate with Pd(II) via sulfur and nitrogen atoms. Meanwhile, the **PdTH2** is suggested to coordinate with Pd(II) via sulfur and oxygen atoms. For thiazole complex of **HgTD6**, the molecular structure from single crystal X-ray diffraction analysis shows the coordination of Hg(II) metal is via nitrogen atom in the thiazole ring. The investigations catalytic activities of **PdTH1**, **PdTH2** and **PdTH3** as metal catalysts in several Heck Cross-coupling reactions reveal the excellence performance of **PdTH3** as catalyst and this complex gave better conversion of reactant to product when compared to with the application of $PdCl_2$ and $Pd(OAc)_2$ as catalysts in the same Heck Cross-coupling reaction.

Abstrak tesis yang dikemukakan kepada Senat Universiti Malaysia Terengganu sebagai memenuhi keperluan untuk ijazah Master Sains.

SINTESIS DAN PENCIRIAN BEBERAPA KOMPLEKS TIOUREA-TIAZOL SEBAGAI PEMANGKIN HOMOGEN DALAM TINDAK BALAS GANDING-SILANG HECK

SITI AISHAH BINTI ZAKARIA

September 2011

Pengerusi : **Mohd Sukeri Mohd Yusof, Ph.D.**

Ahli : **Wan Mohd Khairul Wan Mohamed Zin, Ph.D.**

Fakulti : **Sains dan Teknologi**

Terbitan tiourea merupakan sebatian yang boleh direka bentuk dengan menambah kumpulan gantian pada terminal atom nitrogen. Terbitan ini berupaya untuk berkoordinat bersama logam dengan pelbagai mod koordinatan dan kompleks ini telah diaplikasikan dalam pelbagai bidang. Dalam kajian ini, pengkompleksan Pd(II) dengan ligan tiourea-tiazol telah dilakukan bagi mengetahui tingkah laku pemangkinanya di dalam tindak balas Ganding-silang Heck sebagai pemangkin. Tindak balas antara aril isotiosianat dengan 2-aminobenzotiazol menghasilkan campuran dua sebatian iaitu tiourea-tiazol dan tiazol. Walaubagaimanapun, apabila alkil isotiosianat bertindak balas dengan 2-aminobenzotiazol hanya sebatian tiazol terbentuk. Enam sebatian tiourea-tiazol (**TH1-TH3**, **TH8-TH10**) dan sepuluh sebatian tiazol (**TD1-TD10**) telah berjaya disintesis. Empat ligan terpilih telah berjaya dilakukan pengkompleksan di dalam kajian ini dengan Pd(II) (**PdTH1**, **PdTH2**, **PdTH3**) dan Hg(II) (**HgTD6**). Semua sebatian telah dicirikan oleh kaedah spektroskopi dan analisis yang biasa iaitu Fourier Pertukaran Inframerah (FTIR), ^{1}H dan ^{13}C Resonan Magnetik Nukleus (^{1}H dan ^{13}C NMR), analisis mikrounsur (CHNS) dan penentuan takat lebur. Struktur molekul bagi lima ligan yang disintesis (**TH2**, **TH10**, **TD1**, **TD8** dan **TD10**) dan kompleks **HgTD6** telah dikenalpasti dengan menggunakan analisis pembelauan hablur tunggal kristalografi sinar-X. Spektrum FTIR ligan menunjukkan regangan penting bagi kumpulan berfungsi ν(N-H), ν(C=O), ν(C=N) dan ν(C-N) masing-masing pada lingkungan 3300 cm^{-1}, 1600 cm^{-1}, 1500 cm^{-1} dan 1400 cm^{-1}. Manakala bagi regangan di lingkungan 700 cm^{-1} ditetapkan untuk regangan ν(C=S) bagi sebatian tiourea-tiazol. Dalam spektra ^{1}H NMR, pembentukan bahagian tiourea di dalam sebatian tiourea-tiazol telah terbukti berdasarkan kehadiran dua isyarat NH pada δ_H 12.18-12.66 (–N**H**C=O) dan δ_H 13.95-14.28 (–N**H**C=S). Bagi sebatian tiazol isyarat NH muncul pada δ_H 12.03-12.72 ppm

(–N**H**C=O). Manakala, dalam spektra ^{13}C NMR, isyarat untuk karbon karbonil and karbon tion bagi sebatian tiourea-tiazol masing-masing berada pada δ_C 166.19-170.56 ppm dan δ_C 177.71-182.11 ppm. Sebaliknya, isyarat karbon karbonil bagi sebatian tiazol boleh dilihat pada lingkungan δ_C 150 ppm. Analisis pembelauan tunggal sinar-X bagi ligan **TH2** dan **TH10** menunjukkan kedua-dua sebatian mempunyai konfigurasi *cis-trans* dengan kedudukan benzotiazol dan kumpulan benzoil merujuk kepada atom tion S, pada ikatan C-N masing-masing. Di satu sudut yang lain, spektra FTIR untuk kompleks **PdTH1**, **PdTH2** dan **PdTH3** menunjukkan anjakan yang jelas terhadap frekuensi mereka dengan ν_Δ 3-115 cm^{-1} berbanding dengan ligan. Sementara itu FTIR kompleks bagi **HgTD6** dan ligannya (**TD6**) menunjukkan tiada perubahan yang jelas di dalam spektra mereka. Pengkoordinatan logam Pd(II) terhadap ligan dicadangkan berdasarkan isyarat yang paling teranjak di dalam ^{13}C NMR. Kompleks bagi **PdTH1** dan **PdTH3** dicadangkan berkoordinat melalui atom sulfur dan nitrogen dengan Pd(II). **PdTH2** dicadangkan berkoordinat melalui atom sulfur dan oksigen dengan Pd(II). Bagi kompleks **HgTD6**, struktur molekul daripada analisis pembelauan hablur tunggal kristalografi sinar-X menunjukkan pengkoordinatan logam Hg(II) adalah melalui atom nitrogen di dalam gelang tiazol. Aktiviti pemangkinan oleh **PdTH1**, **PdTH2** dan **PdTH3** sebagai logam-pemangkin di dalam beberapa tindak balas Ganding-silang Heck menunjukkan pencapaian yang cemerlang oleh **PdTH3** sebagai mangkin dan kompleks ini memberikan penukaran bahan pemula kepada hasil yang lebih baik berbanding dengan penggunaan $PdCl_2$ dan $Pd(OAc)_2$ sebagai mangkin di dalam tindak balas Ganding-silang Heck yang sama.