

SYNTHESIS AND CHARACTERIZATION OF
PALLADIUM (II) PIVALOYL THIOUREA
COMPLEXES AS HOMOGENEOUS CATALYSTS IN
SONOGASHIRA CROSS COUPLING REACTION

FALYNEE FAHA BINTI ABDUL WAHAB

MASTER OF SCIENCE
UNIVERSITI MALAYSIA TERENGGANU
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complexes as homogeneous catalysts in sonogashira cross
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**Thesis Submitted in Fulfillment of the Requirement for
the Degree of Master of Science in the Faculty of
Science and Technology
Universiti Malaysia Terengganu**

March 2013

*This thesis is dedicated with
deepest love and affection
to my everything,
my beloved Papa and Mama
for their love, patience and strength
have inspired me to be the best I can be.*

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 CHARACTERIZATION OF PALLADIUM (II) PIVALOYL
THIOUREA COMPLEXES AS HOMOGENEOUS CATALYSTS IN
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FALYNEE FAHA BINTI ABDUL WAHAB

March 2013

**Main Supervisor : Associate Professor Wan Mohd Khairul Bin Wan
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Faculty : Science and Technology

Thiourea derivatives are gaining prominence due to its versatility as a ligand, insensitivity to air and moisture and can be designated by varying substituents on the nitrogen atoms. The coordination ability to transition metals has attracted interest to widely applied the derivatives in numerous fields. In this study, palladium (II) complexes featuring pivaloylthiourea derivatives were synthesized in order to evaluate their catalytic behavior in Sonogashira cross coupling reaction as homogeneous catalyst. The reaction between pivaloyl isothiocyanate with various amines have resulted pivaloylthiourea derivatives ligands with general formula $(\text{CH}_3)_3\text{C}(\text{O})\text{NHC}(\text{S})\text{NHR}$, with different substituted groups such as NO_2 (**L1**), OMe (**L2**) and H (**L3**). The complexation of all synthesized ligands with Pd (II) (**MC1**, **MC2**, **MC3**) have been successfully designated. All synthesized compounds were characterized by typical

spectroscopic and analytical methods namely Fourier Transform Infrared (FTIR), ^1H and ^{13}C Nuclear Magnetic Resonance (NMR), UV-Visible analysis, microelemental analyses (CHNS) as well as melting point determination. The FTIR spectra of the ligands show the bands of interest such as $\nu(\text{N-H})$, $\nu(\text{C=O})$, $\nu(\text{C-N})$ and $\nu(\text{C=S})$ which can be observed at around $3036\text{-}3290\text{ cm}^{-1}$, $1666\text{-}1678\text{ cm}^{-1}$, $1324\text{-}1326\text{ cm}^{-1}$ and $736\text{-}743\text{ cm}^{-1}$ respectively. In addition, the $\nu(\text{NO}_2)$ in **L1** is observed as strong intensity band at 1513 cm^{-1} . On the contrary, the FTIR spectra of the complexes, **MC1**, **MC2** and **MC3** shown significant shift in their frequencies with ν_{Δ} $5\text{-}173\text{ cm}^{-1}$ compared to the free ligands. In ^1H NMR spectra, the signals of δ_{H} (N_1H) and δ_{H} (N_2H) are presence at around δ_{H} $8.58\text{-}8.60\text{ ppm}$ and δ_{H} $12.33\text{-}13.00\text{ ppm}$ respectively. Whilst, in ^{13}C NMR, the signal of carbonyl carbon can be seen at δ_{C} $178.35\text{-}178.76\text{ ppm}$ and carbon thione appeared at δ_{C} $179.41\text{-}179.87\text{ ppm}$. The coordination of ligand towards Pd(II) metal center is suggested based on the most shifted signal recorded in ^1H NMR. Thus, all complexes are proposed to coordinate to the metal center via sulfur and oxygen atoms. The investigation of catalytic activity of all metal complexes as homogeneous catalysts in several Sonogashira cross coupling reactions has revealed **MC3** as the best catalyst as it gave highest conversion of reactant to product when compared to **MC1** and **MC2**. Further optimization on catalyst loadings and effect of bases were carried out to determine the best reaction condition.

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sebagai memenuhi keperluan untuk ijazah Master Sains

**SINTESIS DAN PENCIRIAN KOMPLEKS PALADIUM (II) TIOUREA
PIVALOIL SEBAGAI MANGKIN HOMOGEN DALAM TINDAK
BALAS GANDING SILANG SONOGASHIRA**

FALYNEE FAHA BINTI ABDUL WAHAB

Mac 2013

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Terbitan tiourea semakin dikenali kerana keserba-bolehan sebagai ligan, tidak sensitif kepada udara dan kelembapan serta dapat ditukar pelbagai kumpulan pengganti pada atom nitrogen. Keupayaan terbitan tiourea untuk berkoordinat dengan logam-logam peralihan telah mendapat perhatian meluas untuk digunakan dalam pelbagai bidang. Dalam kajian ini, kompleks paladium (II) menampilkan terbitan-terbitan pivaloiltiourea telah disintesis untuk dinilai tingkah laku sebagai pemangkin homogen dalam tindak balas ganding silang Sonogashira. Tindak balas antara pivaloil isotiosianat dengan pelbagai amin telah menghasilkan ligan terbitan pivaloiltiourea yang mempunyai formula am $(\text{CH}_3)_3\text{C}(\text{O})\text{NHC}(\text{S})\text{NHR}$, dengan pelbagai kumpulan pengganti seperti NO_2 (**L1**), **OMe** (**L2**) and **H** (**L3**). Pengkompleksan ligan yang disintesis dengan paladium (II) (**MC1**, **MC2**, **MC3**) telah berjaya dihasilkan. Semua sebatian telah dicirikan dengan kaedah spektroskopi dan analisis yang biasa iaitu Fourier Pertukaran Merah (FTIR), ^1H

dan ^{13}C Resonan Magnetik Nukleus, Ultralembayung Sinar Nampak (UV-Vis), analisis mikrounsur (CHNS) dan juga penentuan takar lebur. Spektrum FTIR ligan menunjukkan regangan penting bagi kumpulan berfungsi $\nu(\text{N-H})$, $\nu(\text{C=O})$, $\nu(\text{C-N})$ dan $\nu(\text{C=S})$ masing-masing dapat diperhatikan pada lingkungan $3036\text{-}3290\text{ cm}^{-1}$, $1666\text{-}1678\text{ cm}^{-1}$, $1324\text{-}1326\text{ cm}^{-1}$ dan $736\text{-}743\text{ cm}^{-1}$. Manakala, regangan kumpulan berfungsi $\nu(\text{NO}_2)$ untuk **L1** dilihat sebagai berkeamatan kuat pada 1513 cm^{-1} . Di satu sisi yang lain, spektra FTIR untuk kompleks, **MC1**, **MC2** dan **MC3** menunjukkan anjakan yang jelas terhadap frekuensi mereka dengan $\nu_{\Delta}\text{ }5\text{-}173\text{ cm}^{-1}$ berbanding dengan ligan bebas. Dalam spektra ^1H NMR, kehadiran isyarat $\delta_{\text{H}}(\text{N}_1\text{H})$ dan $\delta_{\text{H}}(\text{N}_2\text{H})$ adalah masing-masing pada sekitar $8.58\text{-}8.60\text{ ppm}$ dan $\delta_{\text{H}}\text{ }12.33\text{-}13.00\text{ ppm}$. Sementara itu, dalam ^{13}C NMR, isyarat karbon karbonil hadir pada $\delta_{\text{C}}\text{ }178.35\text{-}178.76\text{ ppm}$ manakala isyarat karbon tion pada $\delta_{\text{C}}\text{ }179.41\text{-}179.87\text{ ppm}$. Koordinasi ligand kepada logam peralihan paladium (II) dicadang berdasarkan anjakan yang paling ketara dalam ^1H NMR. Justeru, semua kompleks dicadang berkoordinat melalui atom sulfur dan oksigen. Penyiasatan aktiviti pemangkin bagi semua kompleks sebagai pemangkin homogen dalam beberapa tindak balas ganding silang Sonogashira telah mendedahkan **MC3** sebagai pemangkin terbaik kerana kompleks ini memberikan penukaran bahan pemula kepada hasil yang tinggi berbanding dengan **MC1** dan **MC2**. Optimisasi seterusnya dijalankan ke atas kuantiti pemangkin dan kesan alkali untuk menentukan keadaan tindakbalas yang terbaik.