

**SYNTHESIS, CHARACTERIZATION AND CATALYTIC ACTIVITY OF
PALLADIUM(II) AROYLHYDRAZONE COMPLEXES IN MIZOROKI-
HECK REACTION**

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Special dedication to my parents, family and friends for their support and love.

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ABSTRACT

The palladium catalyzed Mizoroki-Heck reaction represents one of the most important methods for the formation of carbon-carbon bond in organic synthesis. The application of palladium(II) Schiff base complexes as homogenous catalyst have gained interest due to their high stability and flexibility. This dissertation reports on the synthesis, characterization and catalytic activity performance of new palladium(II) aroylhydrazone complexes in the homogenous Mizoroki-Heck cross-coupling reaction under optimum condition. Two new aroylhydrazone ligands have been synthesized by condensation reaction between salicyloylhydrazide with 2-acetylpyridine and 2-benzoylpyridine in a 1:1 molar ratio. The corresponding palladium(II) complexes were synthesized by treating the ligands with one mole equivalent of bis(benzonitrile)palladium(II) chloride at room temperature. All the obtained products were fully characterized by FTIR, $^1\text{H-NMR}$ and UV-Vis spectroscopic techniques. The spectroscopic data revealed that the aroylhydrazone ligands acted as monobasic tridentate donor, coordinating through the enolic oxygen, imine nitrogen and pyridyl nitrogen atoms to the palladium $^{2+}$ ion. The performance of the palladium(II) complexes as homogeneous catalysts were evaluated in the Mizoroki-Heck reaction of arylbromide with methyl acrylate in the presence of triethylamine as base and *N,N*-dimethylacetamide as solvent at 120 °C. Both catalysts gave the conversion of 4-bromoacetophenone up to 100% after 24 hours with almost 100% selectivity of the expected *trans*-methyl 3-(4-acetylphenyl)acrylate.

ABSTRAK

Tindak balas Mizoroki-Heck bermangkinkan kompleks paladium(II) merupakan salah satu kaedah yang paling penting untuk pembentukan ikatan karbon-karbon dalam organik sintesis. Aplikasi kompleks paladium(II) bes Schiff sebagai pemangkin homogen telah menarik minat kerana kestabilan yang tinggi dan fleksibel. Disertasi ini melaporkan mengenai sintesis, pencirian dan pencapaian aktiviti pemangkinan bagi kompleks paladium(II) aroilhidrazon yang baru dalam tindak balas homogen ikatan karbon-karbon Mizoroki-Heck pada keadaan optimum. Dua ligan baru aroilhidrazon telah disintesis melalui tindak balas kondensasi antara saliseloihidrazida dengan 2-asetilpiridina dan 2-benzoilpiridina dalam nisbah molar 1:1. Kompleks paladium(II) yang sepadan telah disintesis melalui tindak balas antara ligan aroilhidrazon dan bis(benzonitril)paladium(II) klorida dalam nisbah satu mol yang setara pada suhu bilik. Kesemua produk yang diperolehi, dicirikan sepenuhnya menggunakan teknik spektroskopi FTIR, ^1H -NMR dan UV-Vis. Data spektroskopi mendedahkan bahawa ligan aroilhidrazon bertindak sebagai penderma tridentat monobes yang terkoordinat melalui atom oksigen enol, nitrogen imina dan nitrogen pyridil pada ion paladium $^{2+}$. Prestasi kompleks paladium(II) sebagai pemangkin homogen telah dinilai dalam tindak balas Mizoroki-Heck antara arilbromida dengan metil akrilat dengan bantuan trietilamina sebagai bes dan *N,N*-dimetilasetamida sebagai pelarut pada 120 °C. Kedua-dua pemangkin memberikan penukaran 4-bromoasetofenon sebanyak 100% selepas 24 jam dengan hampir 100% pemilihan terhadap *trans*-metil 3-(4-asetilfenil)akrilat yang dijangkakan.