CHAPTER 2

CATALYSIS OF HECK REACTION
This chapter is divided into two sections

Section 1. Nickel (0) and Cu (I) catalyzed reactions of aryl and vinyl halides with olefins and alkynes.

Introduction and Background

The development of new catalysts for C-C bond formation reaction is a challenging area in organic synthesis. There are many reactions in which the C-C bond is formed by catalysis of various transition metal complexes. The most important reaction in which the facile and selective C-C bond formation is constructed is known as the Heck reaction, catalyzed by palladium complexes, described in the last chapter. Similar reaction catalyzed by the other transition metal complexes and transition metal salts will be described briefly below.

Styrene was prepared by the reaction of chlorobenzene with ethylene in the presence of nickel salts, triarylphosphine and zinc as shown in scheme-1.\(^1\)

Scheme-1

\[
\text{Cl} + \text{CH}_2=\text{CH}_2 \xrightarrow{\text{Ni salts \ PPh}_3, \text{Zn}} \text{CH}=	ext{CH}_2
\]

Boldrini et al. reported the use of RhCl(PPh\(_3\))\(_3\), Ni(PPh\(_3\))\(_4\), [Rh(COD)(PPh\(_3\))\(_2\)] PF\(_4\) for the reaction of vinyl halides with alkali salts of 3-butenolic acids to furnish dienoic acids containing 3, 5 conjugated double bonds (scheme-2).\(^2\)

Scheme-2

\[
\text{Br} + \text{CH}=	ext{CH}-\text{COOH} \xrightarrow{\text{Catalyst \ EtOH, 85 }^\circ\text{C} \ \text{2-48 h}} \text{CH}=	ext{CH}-\text{COOH}
\]
The reactions of aryl and vinyl halides with activated olefins in the presence of catalytic amount of NiCl$_2$(PPh$_3$)$_2$ and excess of zinc powder in tetrahydrofuran gave the coupled products (scheme-3).

**Scheme-3.**

\[
\begin{align*}
\text{NiCl}_2(P\text{Ph}_3)_2 + \text{CH}_2=\text{CHR}_1 & \rightarrow \text{CH}_2=\text{CHR}_1\text{Ni}(\text{PPh}_3)_2 \\
\text{RX} + \text{CH}_2=\text{CHR}_1 & \rightarrow \text{R-CH} = \text{CHR}_1 + \text{R-CH}_2 \text{CH}_2 \text{-R}_1 + \text{R-} \text{R}_1
\end{align*}
\]

R= aryl, vinyl

S. A. Lebedev et al. studied the effective catalytic system for the activation of aryl and alkyl bromides with styrene and methyl acrylate to give stilbenes and cinnamates respectively (scheme-4).

**Scheme-4**

\[
\begin{align*}
\text{R-Br} + \text{CH}_2=\text{CH}-\text{C}_6\text{H}_5 & \rightarrow \text{RCH}_2\text{CH}_2\text{Ph} \\
\text{R-Br} + \text{CH}_2=\text{CH}-\text{COOMe} & \rightarrow \text{RCH}_2\text{CH}_2\text{COOMe}
\end{align*}
\]

R= aryl, alkyl  L=PP$_3$

Sustmann et al. reported the reaction of alkyl halides, aryl and vinyl halides with electron deficient olefins catalyzed by NiCl$_2$.6H$_2$O in the presence of zinc and pyridine in tetrahydrofuran to give the conjugate addition product (scheme-5).

**Scheme-5**

\[
\begin{align*}
\text{R-X} + \text{CH}_2=\text{CH}-\text{COOEt} & \rightarrow \text{RCH}_2\text{CH}_2\text{COOEt} \\
\end{align*}
\]

R= alkyl, aryl and vinyl
S. Iyer reported the vinylation of aryl iodides catalyzed by CoCl(PPh$_3$)$_2$, RhCl(PPh$_3$)$_2$, and IrClCO(PPh$_3$)$_2$ to give the corresponding cinnamates and stilbenes in high yield using K$_2$CO$_3$ and N-methyl pyrrolidinone (scheme-6).\(^5\)

**Scheme-6**

\[
\begin{align*}
\text{W} &= \text{C}_6\text{H}_5, \text{COOR} \\
\text{W} &= \text{C}_6\text{H}_5, \text{Ph}
\end{align*}
\]

Vinylolation of aryl iodides using Pt(COD)Cl$_2$/PPh$_3$ as a catalytic system was studied by Kelkar and it was found that dehalogenated products were formed in the reaction in presence of organic base (scheme-7).\(^7\)

**Scheme-7**

Kelkar *et al.* reported the vinylation of 4-bromo-4'-hydroxybiphenyl with ethyl acrylate in the presence of NiCl$_2.6\text{H}_2\text{O}$, PPh$_3$ and organic base to afford ethyl 4-(4'-hydroxyphenyl) cinnamate with high selectivity (98%) (Scheme-8).\(^8\)

**Scheme-8**
A detailed study on the copper catalyzed condensation of 2-bromobenzoic acids with \( \beta \)-dicarbonyl anions to \( \alpha \)-arylated-\( \beta \)-dicarbonyl compounds in high yield reported by A. Mckillop et al. is shown in scheme-9.
OBJECTIVE

The aim was to develop new catalysts for the coupling reactions of aryl and vinyl halides with olefins, alkynes, carbon and nitrogen nucleophiles based on the oxidative addition and reductive elimination properties of the transition metal complexes and salts.

PRESENT WORK

Our present study involves the investigation of new catalysts for the Heck reaction. Some of the transition metal complexes which are in lower oxidation state can easily undergo ligand dissociation, oxidative addition and reductive elimination reactions. Our initial study was on the reactions of aryl iodides with olefins, catalyzed by the low valent nickel complexes for example, Ni[P(OPh)₃]₄ and Ni[P(OEt)₃]₄ which affords the expected Heck type coupling products, stilbenes and cinnamates is shown in scheme-10. The reaction of aryl iodide with alkyne in the presence of Ni[P(OPh)₃]₄ was also carried out (Sonagashira coupling) (Scheme-11).

Scheme-10

\[
\begin{align*}
R^+ + W &\rightarrow \text{Ni[P(OPh)₃]₄, K₂CO₃} \\
&\text{NMP, 150°C, Ar} \\
R = \text{OCH₃, Cl} &\text{ W = Ph, COOEt etc.}
\end{align*}
\]

Scheme-11
Some of the transition metal salts, say copper iodide and copper bromide are known to catalyze the reactions of aryl halides with various carbon and heteroatom nucleophile. The reactions of aryl iodides with olefins catalyzed by copper iodide and copper bromide in the presence of potassium carbonate were carried out to form the expected coupling products in good yield by using both stoichiometric and catalytic amount of copper salts (scheme-12).

Scheme-12

\[
\begin{align*}
\text{R}^1 &= \text{CHO}, \text{COOEt}, \text{R}^2 = \text{H}, \text{CH}_3 \\
\text{X} &= \text{Br}, \text{I} \\
\end{align*}
\]

The reaction of vinyl halide (β-bromostyrene) with olefins in the presence of nickel (0) complexes and copper salts have been carried out (scheme-13).

Scheme-13

\[
\begin{align*}
\text{W} &= \text{Ph}, \text{COOEt} \\
\text{Ni}(0) &= \text{Ni(P(OPh)}_3)_4, \text{Ni(P(OEt)}_3)_4 \\
\text{Cu(I)} &= \text{CuI, CuBr} \\
\end{align*}
\]

The precursors for intramolecular Heck reaction were synthesized from o-iodobenzoic acid by the following reaction sequences shown in scheme-14.10

Scheme-14
The intramolecular Heck reactions of allyl-2-iodobenzoate, 1\textit{N}-allyl-2-iodobenzamide and 1\textit{N}-allyl-1\textit{N}-methyl-2-iodobenzamide catalyzed by Ni\{P(OPh)\}_4 and copper salts in the presence of potassium carbonate were performed to get the corresponding heterocyclic compounds (scheme-15 and 16).

\textbf{Scheme-15}

\begin{align*}
& \text{Ni}(0) = \text{Ni}\{P(OPh)\}_4, \quad \text{Ni}\{P(OEt)\}_4 \\
& \text{Cu(1)} = \text{CuI, CuBr}
\end{align*}

\textbf{Scheme-16}

\begin{align*}
& \text{Ni}(0) = \text{Ni}\{P(OPh)\}_4, \quad \text{Ni}\{P(OEt)\}_4 \\
& \text{Cu(1)} = \text{CuI, CuBr}
\end{align*}
The reactions of 4-iodoanisole with vinyl ketones, carbon and nitrogen nucleophiles catalyzed by Ni[P(OPh)]₄ and Cul have been carried out with various modifications of reaction conditions (scheme 17 and 18).

Scheme-17

\[
\text{CH}_3\text{O}^+\quad \overset{\text{COOR}}{\underset{\text{Ni[P(OPh)]₄, K}_2\text{CO}_3}{\text{Base, Solvent}}} \quad \overset{\text{Base, Solvent}}{\underset{100-150^\circ C}{\text{CH}_3\text{O}}} \quad \text{R}_1 = \text{CN, COOEt} \\
\text{R} = \text{Et} \\
\text{Base} = \text{NaH, K}_2\text{CO}_3 \\
\text{Solvent} = \text{Dioxane, NMP}
\]

Scheme-18

\[
\text{CH}_3\text{O}^-\quad \overset{\text{COOR}}{\underset{\text{Cul, K}_2\text{CO}_3}{\text{NMP, 150^\circ C, Ar}}} \quad \overset{\text{NMP, 150^\circ C, Ar}}{\underset{\text{CH}_3\text{O}}{\text{R} = \text{CH}_3, \text{CH}_2\text{CH}_3, \text{C}_9\text{H}_6}}
\]

The results of inter and intramolecular reactions of aryl and vinyl halides with olefins and alkynes catalyzed by Ni[P(OPh)]₄ and Cul are summarized in Table-1 and Table-2.
<table>
<thead>
<tr>
<th>S.No</th>
<th>Aryl/Vinyl halide</th>
<th>Olefin/Alkyne</th>
<th>Time (h)</th>
<th>Product</th>
<th>Yield %</th>
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<tbody>
<tr>
<td>1</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>=C=COOEt</td>
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Table 2: CuI catalyzed reactions of aryl and vinyl halides with olefins

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<tr>
<th>S.No</th>
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<th>Olefin/Alkyne</th>
<th>Time (h)</th>
<th>Product</th>
<th>Yield %</th>
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</tbody>
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RESULTS AND DISCUSSION

The starting materials required for the Heck type coupling reactions were prepared by the literature methods and characterized by the usual spectroscopic techniques. The inter and intramolecular reactions of aryl and vinyl halides with olefins and alkynes catalyzed by Ni(0) complex and Cu(I) salts afforded the Heck type coupling products in good yield. The Ni[P(Ph)3]4 complex was synthesized according to the literature method. The precursors (4 & 5) for intramolecular Heck reaction were synthesized from o-iodobenzoic acid. The IR spectrum of the starting material, allyl 2-iodobenzoate (4) showed a sharp peak at 1732 cm⁻¹ which indicating the presence of carbonyl group of ester. The ¹H NMR spectrum displayed a doublet at δ 8.0 with J = 8.8 Hz corresponding to one of the aromatic proton at 5th carbon and another doublet at δ 7.8 with J = 8.0 Hz confirmed the presence of proton at 3rd carbon. The other two aromatic protons appeared as multiplets at δ 7.4-7.25 and 7.15-7.0. A multiplet at δ 6.1-5.9 appeared indicating the presence of internal olefinic proton and the two terminal olefinic protons appeared as doublets, one at δ 5.5 with J = 17.6 Hz and another at δ 5.2 with J = 8.8 Hz. The ¹³C NMR spectrum revealed the two methylenic carbons signals at δ 94.15 and 66.10 corresponding to olefinic and methylenic carbon adjacent to oxygen which was identified by DEPT experiments. The mass spectrum displayed a molecular ion peak at m/z 288. All the above data confirmed the structure of 4. Similarly the structure of 1N-allyl-1N-methyl-2-iodobenzamide (5) was also confirmed. The inter and intramolecular reactions of aryl and vinyl halides with olefins and alkynes catalyzed by Ni(0) complex gave the Heck type coupling products in good yield. The reaction of 4-idoanisole with styrene catalyzed by Ni[P(Ph)3]4 afforded two products (regioisomers) and characterized by IR, ¹H NMR and mass spectra. The IR spectrum of both the products showed a prominent peak at 1600 cm⁻¹ indicating the presence of C=C of the olefinic systems. The ¹H NMR spectrum of one of the isomer showed a doublet at
δ 6.9 with coupling constant $J = 12.1$ Hz confirmed the presence of olefinic proton of *trans* product. The mass spectrum showed a molecular ion peak at m/z 210 supporting the formation of the expected product. These above data confirmed the structure of the product, 1-(4-methoxyphenyl)-2-phenyl-(E)-ethylene. The $^1$H NMR spectrum of the other isomer showed two singlets, one at δ 4.95 and another singlet at δ 4.90 due to the presence of terminal olefinic protons. The IR spectrum of the product obtained from the reaction of 4-chloroiodobenzene with ethyl acrylate showed strong absorption bands at 1705 cm$^{-1}$ and 1600 cm$^{-1}$ which indicating the presence of carbonyl group and C=O of α, β-unsaturated systems. The $^1$H NMR spectrum of the product displayed two doublets; one at δ 6.3 ($J = 17.2$ Hz) and another at δ 7.6 ($J = 17.2$Hz) which assigned to olefinic protons of the unsaturated esters and its trans stereochemistry. The mass spectrum of product showed a molecular ion peak at (m/z) 210, which supports the structure of the expected product.

The IR spectrum of the product obtained from the copper iodide catalyzed reaction of 4-iodoanisole with methacrolein gave a sharp peak at 1660 cm$^{-1}$. The $^1$H NMR spectrum displayed a singlet at δ 9.5 due to the presence of aldehyde proton and two doublets at δ 7.5 and 7.0 confirming the aromatic protons of $A_2B_2$ pattern. A singlet appeared at δ 7.2 corresponding to olefinic proton. Two sharp singlets at 3.85 and 2.1 could be assigned to methoxy and allylic methyl protons. The mass spectrum showed a molecular ion peak at m/z 176, which supporting the structure of the product (12). Similarly the structure of the product (17) obtained from the reaction of 4-iodoanisole with methylmethacrylate was also confirmed.

The $^1$H NMR spectrum (shown in page 54) of the product formed from the reaction of 4-iodoanisole with cyclooctene displayed two doublets at δ 7.3 and 6.8 which assigned to aromatic protons of $A_2B_2$ type. A triplet appeared at δ 5.8 indicating the presence of olefinic proton and a singlet 3.85 due to the presence of methoxy protons. A triplet at δ 2.6 was assigned for allylic
methylene protons and a multiplet at $\delta$ 2.25-2.15 was attributed to the other methylenic protons. A multiplet appeared at $\delta$ 1.55-1.45 corresponding to eight methylenic protons. The mass spectrum showed a molecular ion peak at m/z 216. The above data confirmed the structure of the product (14).

The intramolecular reaction of 1N-allyl-1N-methyl-2-iodobenzamide catalyzed by both Ni[P(OPh)$_3$]$_4$ and copper iodide gave the expected cyclised product, 2, 4-dimethylisoquinolinone in 79% and 54% yield respectively. IR spectrum of the product showed sharp peaks at 1699 cm$^{-1}$ and 1626 cm$^{-1}$ for C=O and C=C respectively which indicating the formation of the cyclised product. In the $^1$H NMR spectrum, a singlet at $\delta$ 2.25 assigned to allylic methyl and a singlet at $\delta$ 6.9 was assigned to the proton on heterocyclic ring of the product. A doublet at $\delta$ 8.5 corresponding to the proton of the aromatic ring, which is periplanar to the carbonyl. The $^{13}$C NMR spectrum revealed all the carbon signals of the product and matching with literature.$^{13}$ The carbonyl carbon appeared at $\delta$ 162.02 and two signals at $\delta$ 36.39 and 15.00 confirmed the presence of N-methyl and allylic methyl respectively. Both $^1$H NMR and $^{13}$C NMR spectra shown in page 55. The mass spectrum displayed a molecular ion peak at (m/z) 173 supporting the formation of cyclised product, 2, 4-dimethylisoquinolinone.

The reaction of allyl-2-iodobenzoate catalyzed by the Ni(0) complex gave dehalogenated product and Cul afforded the dehalogenated and deallylated product which was evidenced by the $^1$H NMR and Mass spectra. The reactions of $p$-iodoanisole with vinyl ketones, cyclohexenone, benzalacetone and cyclooctene catalyzed by copper salts were unsuccessful, the reason is that vinyl ketones are easily polymerized before it reacts with the metal complexes in the reaction medium. Similarly, Ni[P(OPh)$_3$]$_4$ catalyzed reaction of $p$-iodanisole with carbon and nitrogen nucleophiles were found to be unsuccessful under various modified reaction conditions.
In conclusion, we have found transition metal complex, Ni[P(OPh)₃]₄ and transition metal salt copper iodide as new alternative catalysts to catalyze the coupling reaction of aryl iodide and vinyl bromides with olefins (Heck reaction) and alkynes at high temperature.

EXPERIMENTAL

General

All commercial reagents were obtained from Aldrich Chemical Co., S. D. Fine Chemical Co. India and LOBA Chemical Co. India. Progress of the reaction was monitored by TLC and was visualized by UV absorption by fluorescence quenching or I₂ staining or by both. Silica gel 60-120 and 100-200 mesh obtained from S. D. Fine Chemical Co. India and Rico Industrial Chemicals Co. India for column chromatography.

All melting points were uncorrected in degree Celsius and were recorded on a Thermonik melting point apparatus. IR spectra were recorded on a perkin-Elmer infrared spectrometer model 599-B and model 1620 FT-IR. ¹H NMR spectra were recorded using TMS as internal reference on Bruker AC-200, Bruker MSL-300 and Bruker -500 instruments using CDCl₃ as solvent. Chemical shifts are reported in δ. ¹³C NMR spectra were recorded on Bruker AC-200 and Bruker MSL-300 instruments operating at 50.32 MHz and 75.3 MHz, respectively. Mass spectra were recorded on Finnigan-Mat 1020C mass spectrometer and are obtained at an ionization potential of 70 eV.

Preparation of Ni[P(OPh)₃]₄

A mixture of nickel nitrate (0.76 g, 4.4 mmol) and triphenyl phosphite (3.9 g, 13 mmol) in ethanol (10 mL) was charged into a 50 mL conical flask. To this stirred solution, sodium boro
hydride (0.25 g, 6.94 mmol) in warm ethanol (10 mL) was added slowly for 10 minutes. The white precipitate obtained was filtered, washed with ethanol and dried. M. P: 145 °C.

Recrystallisation of Copper iodide

Copper iodide (1.9 g, 100 mmol) was charged into a 500 mL RB flask equipped with a magnetic stirring bar. To this stirred reaction mixture, potassium iodide solution (70 mL, 3.5 M) was added slowly in about 30 minutes with moderate heating (40-50 °C) followed by addition of charcoal (2.5 g). The mixture was allowed to stir at 45 °C for 1 h. The resulting mixture was filtered through sintered funnel and the filtrate was diluted with water (250 mL). The solution was allowed to stand for 1 h. The precipitated white solid was filtered through a sintered funnel, washed with water, ethanol and ether. The product was dried in a desiccator (calcium chloride).

Synthesis of Aryl and Vinyl halides

The starting materials, aryl iodides were prepared by the literature method from the corresponding aromatic amines by diazotisation followed by addition of potassium iodide and the vinyl bromide prepared from cinnamic acid via bromination, dehydrobromination and decarboxylation sequence.

4-Iodoanisole (I)

Yield : 2.2 g (95%)
Mol. F : C₇H₇IO.
M. P : 51 °C.
IR (Nujol) : 2905 1600, 1410, 1305, 840, 760 cm⁻¹.
¹H NMR (200 MHz,CDCl₃) : δ 7.5 (d, J = 8.7 Hz, 2H), 7.0 (d, J = 8.7 Hz, 2H), 3.85 (s, 3H).
Mass (m/z) : 234 (M+, 61), 219 (16), 128 (12), 105 (19), 97 (44), 55 (100).

4-chloroiodobenzene (2)

Yield : 2.13 g (90%)
Mol. F : C₆H₄ClI
M. P : 52 °C
IR (Nujol) : 3005, 1600, 1480, 1220, 1100, 770 cm⁻¹
¹H NMR (200 MHz, CDCl₃) : δ 7.6 (d, J = 8.1 Hz, 2H), 7.1 (d, J = 8.1 Hz, 2H)

β-Bromostyrene (3)

Mol. F : C₆H₇Br
IR (neat) : 3015, 3000, 1605, 1470, 1280, 940 cm⁻¹
¹H NMR (200, CDCl₃) : δ 7.45 - 7.35 (m, 5H), 7.2 (d, J = 17.0 Hz, 1H), 6.75 (d, J = 17.2 Hz, 1H)

Preparation of Allyl-2-iodobenzoate (4)

A 25 mL RB flask equipped with magnetic stirring bar was charged with o-Iodobenzoic acid (2.48 g, 10 mmol) and 1 mL of thionyl chloride and allowed to stir at room temperature for about 2h. The excess of thionyl chloride was removed by distillation under reduced pressure and the acid chloride stored under argon atmosphere. Another 25 mL two necked RB flask was equipped with magnetic stirring bar, charged with triethylamine (1.01g, 10mmol) and allyl alcohol (0.58g, 10 mmol) in dry dichloromethane (15 mL). To this, freshly prepared acid chloride was added slowly at 0 °C. and the reaction mixture was allowed to stir for 1h. The reaction was quenched using dil. HCl (10% by volume) and the product extracted with
dichloromethane (3×10mL) and the combined organic layer dried over anhydrous sodium sulphate, concentrated under reduced pressure to give the crude product. The crude product was purified by silica gel column chromatography using petroleum ether-ethyl acetate mixture (9: 1)

Yield : 2.72 g (95%)
Mol. F : C_{10}H_{11}I_{2}
IR (Neat) : 1732, 1583, 1429, 1294, 1016, 740 cm⁻¹

H NMR (200 MHz, CDCl₃) : δ 8.0 (d, J = 8.8 Hz, 1H), 7.8 (d, J = 9.0 Hz, 1H), 7.4 (m, 1H), 7.15 - 7.0 (m, 1H), 6.1-5.95 (m, 1H), 5.5 (d, J = 17.6 Hz, 1H), 5.2 (d, J = 8.8 Hz, 1H)

C NMR (50.35 MHz, CDCl₃) : δ 165.85, 141.22, 134.97, 132.43, 130.89, 127.86, 118.76, 94.15, 66.10.

Mass (m/z) : 288 (19), 231 (100), 203 (35), 117 (7), 104 (11), 76 (44).

Preparation of N-allyl-2-iodobenzenamide (5)

A 25 mL RB flask equipped with magnetic stirring bar was charged with o-iodobenzoic acid (2.48 g, 10 mmol) and thionyl chloride (1mL). The reaction mixture was allowed to stir at room temperature for 1h. The excess of thionyl chloride was removed by distillation under reduced pressure. The acid chloride was stored under argon atmosphere. A mixture of triethylamine (1.01g, 10 mmol) and allylamine in dry dichloromethane (15mL) was charged into another 50mL RB flask equipped with magnetic stirring bar. The acid chloride was added slowly at 0° C for 10 minutes and the reaction mixture allowed to stir for 1 h. The reaction was quenched with dil. HCl and the product extracted using dichloromethane (3×10 mL). The combined organic layer was washed with brine solution, dried over anhydrous sodium sulphate.
and concentrated under reduced pressure. The crude product purified by silica gel column chromatography using pet. ether-ethyl acetate mixture (8.5: 1.5).

**Yield**

2.62 g (92%)

**Mol. F**

C₁₀H₁₀INO

**M. P**

120 °C

**IR (CHCl₃)**

3340, 1670, 1600, 1230, 770 cm⁻¹

**¹H NMR (200 MHz, CDCl₃)**

δ 7.8 (d, J = 7.3 Hz, 1H), 7.45 (m, 2H), 7.45 - 7.25 (m, 2H), 7.1 - 7.05 (m, 1H), 6.05 - 5.85 (m, 1H), 5.4 - 5.15 (m, 2H), 4.15 (t, J = 6.0 Hz, 2H)

**Mass (m/z)**

287 (M⁺, 19), 231 (100), 203 (24), 160 (11), 105 (8), 76 (16)

**Preparation of 1N-allyl-1N-methyl-2-iodobenzamide (6)**

A 25 ml two-necked RB flask equipped with magnetic stirring bar and a reflux condenser was charged with sodium hydride (0.58 g, 10 mmol) in dry tetrahydrofuran (10 mL). To this 1N-allyl-2-iodobenzamide in tetrahydrofuran (5 mL) was added slowly at 0°C for 5 minutes followed by addition of methyl iodide (1.072 g, 7.5 mmol). The reaction mixture was allowed to reflux for 3 hours and quenched with ice cold water, the product extracted with ethyl acetate (3x10 mL), dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using pet. ether and ethyl acetate mixture (8.5: 1.5).

**Yield**

1.20 g (80%)

**Mol. F**

C₁₁H₁₂INO

**IR (Neat)**

2986, 1730, 1600, 1040, 740 cm⁻¹

**¹H NMR (200 MHz, CDCl₃)**

δ 7.75 (d, J = 7.5 Hz, 2H), 7.35 - 7.2 (m, 2H), 7.15 - 7.0 (m,
2H), 7.05 - 7.0 (m, 2H), 6.0 - 5.5 (m, 2H), 5.4 - 5.1 (m, 4H),
4.2 (bs, 1H), 3.6 (bs, 1H), 3.05 (s, 3H), 2.75 (s,3H).

$^{13}$C NMR (50.35 MHz, CDCl$_3$) : δ 170.32, 169.92, 142.35, 142.13, 138.75, 132.02, 129.81,
128.12, 127.70, 117.78, 92.37, 91.99, 53.11, 49.08, 35.44,
31.94.

Mass(m/z) : 301 (M$^+$, 16), 231 (100), 203 (43),174 (65), 146 (5), 127 (5),
105 (10), 76 (7).

General procedure for Ni(0) and Cu (I) catalyzed reactions of aryl halides with olefins

Ni(0) Catalyzed reactions of aryl and vinyl halides with olefins and alkynes

A 25 mL RB flask equipped with magnetic stirring bar, reflux condenser and argon
balloon was charged with aryl iodide / vinyl bromide (1mmol), olefin (2.5 mmol) / alkyne (1
mmol), potassium carbonate (0.275 g, 2 mmol) and Ni(P(OPh)$_3$)$_4$ (0.12 g, 10 mol %) in N-
methyl pyrrolidinone (4 mL). The reaction mixture was allowed to stir at 140-150 °C for 12-24
hrs and neutralized with dil. HCl (10% by volume). The product extracted with ethyl acetate (3 x
5 mL), the combined organic extracts was dried over anhydrous sodium sulphate and
concentrated under reduced pressure to yield the crude product. The crude product on silica gel
column chromatographic purification using pet. ether and ethyl acetate mixture gave the pure
products.

CuI Catalyzed reactions of aryl and vinyl halides with olefins

A 25 mL RB flask equipped with magnetic stirring bar, reflux condenser and argon
balloon was charged with aryl iodide / vinyl bromide (1mmol), olefin (2.5 mmol), Potassium
carbonate (0.275 g, 2 mmol) and Cul (0.02 g, 10 mol%) in N-methyl pyrrolidinone (4 mL). The
reaction mixture was allowed to stir at 140-150 °C and neutralized with dil. HCl (10% by
volume). The product was extracted with ethyl acetate (3 x 5 mL), the combined organic extracts
was dried over anhydrous sodium sulphate and concentrated under reduced pressure to yield the
 crude product. The crude product on silica gel column chromatographic purification using pet.
ether and ethyl acetate mixture gave the pure product.

**Ethyl -3-(4-chlorophenyl)-(E)-2-propenoate (7)**

**Mol. F** : C11H11ClO2

**IR (Neat)** : 2980, 1716, 1638, 1592, 1490, 1269, 1173, 883 cm⁻¹

**¹H NMR (200 MHz, CDCl₃)** : δ 7.65 (d, J = 16.2 Hz, 1H), 7.5 (d, J = 8.1 Hz, 2H), 7.4 (d,
J = 8.1 Hz, 2H), 6.4 (d, J = 16.2 Hz, 1H), 4.2 (q, J = 8.0 Hz, 2H), 1.3 (t, J = 8.0 Hz, 3H).

**Ethyl 3-(4-methoxyphenyl)-(E)-2-propenoate (8)**

**Mol. F** : C12H14O2

**IR (Neat)** : 2985, 1710, 1600, 1510, 1240, 1040, 830 cm⁻¹.

**¹H NMR (200 MHz, CDCl₃)** : δ 7.6 (d, J = 17.0 Hz, 1H), 7.5 (d, J = 8.0 Hz, 2H), 6.9 (d, J =
8.0 Hz, 2H), 6.3 (d, J = 17.0 Hz, 1H), 4.2 (q, J = 8.0 Hz, 2H),
3.85 (s, 3H), 1.3 (t, J = 8.0 Hz, 3H)

**¹³C NMR (50.32 MHz, CDCl₃)** : δ 166.9, 161.2, 143.7, 129.5, 127.0, 115.60, 114.11, 60.00,
55.00, 14.17.

**Mass (m/z)** : 206 (M⁺, 100), 191 (1), 178 (6), 161 (19), 154 (30), 135 (9),
126 (20), 98 (63).
1-(4-Methoxyphenyl)-2-phenyl-(E)-ethylene (9)

Mol. F : C₁₅H₁₄O
M. P : 135 °C
IR (CHCl₃) : 2923, 1599, 1375, 1251, 814 cm⁻¹
¹H NMR (200 MHz, CDCl₃) : δ 7.6 - 7.25 (m, 8H), 7.1 (d, J = 17.7 Hz, 1H), 6.9 (d, J = 8.5 Hz, 2H), 3.85 (s, 3H).
Mass(m/z) : 210 (M⁺, 100), 195 (25), 179 (17), 165 (66), 152 (59), 115 (26), 105 (25), 91 (41), 77 (29).

1-(4-Methoxyphenyl)-1-phenylethylene (10)

Mol. F : C₁₅H₁₄O.
IR (CHCl₃) : 2923, 1600, 1453, 1245, 835 cm⁻¹.
¹H NMR (200 MHz, CDCl₃) : δ 7.45 - 7.25 (m, 7H), 6.9 (d, J = 8.5 Hz, 2H), 4.95 (s, 1H), 4.9 (s, 1H), 3.85 (s, 3H).

Ethyl 5-phenyl-(2E, 4E)-2,4-pentadienoate (11)

Mol. F : C₁₃H₁₄O₂
IR (CHCl₃) : 2981, 1708, 1625, 1448, 1367, 1175, 841, 731 cm⁻¹.
¹H NMR (200 MHz, CDCl₃) : δ 7.6 - 7.3 (m, 6H), 6.95 - 6.85 (m, 2H), 6.0 (d, J = 13.0 Hz, 1H), 4.2 (q, J = 8.0 Hz, 2H), 1.3 (t, J = 8.0 Hz, 3H).
Mass(m/z) : 202 (M⁺, 14), 157 (17), 129 (100), 115 (7), 77 (36), 63 (18).

3-(4-Methoxyphenyl)-2-methyl-(E)-2-propenal (12)

Mol. F : C₁₁H₁₂O₂
IR (Neat) : 2920, 1660, 1600, 1320, 1240, 860 cm⁻¹

¹H NMR (200 MHz, CDCl₃) : δ 9.5 (s, 1H), 7.5 (d, J = 8.1 Hz, 2H), 7.2 (s, 1H), 7.0 (d, J = 8.2 Hz, 2H), 3.85 (s, 3H), 2.1 (s, 3H).

Mass (m/z) : 176 (M⁺, 43), 161 (5), 145 (27), 76 (100).

1,4-Diphenyl-(1E,3E)-1,3-butadiene (13)

Mol. F : C₁₆H₁₄

M.P : 151 °C

IR (CHCl₃) : 2985, 1600, 1460, 1230, 780 cm⁻¹

¹H NMR (200 MHz, CDCl₃) : δ 7.6 - 7.25 (m, 10H), 7.2 (d, J = 14.2 Hz, 2H), 6.8 (d, J = 14.2 Hz, 2H)

Mass (m/z) : 206 (M⁺, 13), 130 (49), 104 (100), 91 (89), 77 (54).

1-(4-Methoxyphenyl)-1-cyclooctene (14)

Mol. F : C₁₅H₂₀O

IR (Neat) : 2925, 1601, 1470, 1040, 940, 780 cm⁻¹

¹H NMR (200 MHz, CDCl₃) : δ 7.3 (d, J = 8.0 Hz, 2H), 6.8 (d, J = 8.0 Hz, 2H), 5.8 (t, J = 7.5 Hz, 1H), 3.85 (s, 3H), 2.6 (t, J = 8.5 Hz, 2H), 2.25 - 2.15 (m, 2H), 1.55 - 1.45 (m, 8H)

Mass (m/z) : 216 (53), 188 (98), 201 (11), 173 (40), 159 (42), 134 (36), 128 (31), 121 (59), 115 (65), 91 (59), 77 (4), 65 (31).

1-(4-Methoxyphenyl)-2-phenylacetylene (15)

Mol. F : C₁₅H₁₂O

IR (CHCl₃) : 3057, 2108, 1597, 1487, 1443, 1242, 882 cm⁻¹.
$^1$H NMR (200 MHz, CDCl$_3$) : δ 7.5 - 7.1 (m, 7H), 6.9 (d, $J$ = 8.5 Hz, 2H), 3.85 (s, 3H).

2,4-Dimethyl-1,2-dihydro-1-isoquinolinone (16)

Mol. F : C$_{11}$H$_{11}$NO

M. P : 75 °C

IR (CHCl$_3$) : 2932, 1699, 1626, 1437, 1386, 768 cm$^{-1}$.

$^1$H NMR (200 MHz, CDCl$_3$) : δ 8.5 (d, $J$ = 8.1 Hz, 1H), 7.65 - 7.45 (m, 3H), 6.9 (s, 1H), 3.55 (s, 3H), 2.25 (s, 3H).

$^{13}$C NMR (50 MHz, CDCl$_3$) : δ 162.04, 137.12, 131.61, 130.00, 127.73, 126.32, 125.69, 122.08, 111.64, 36.39, 15.00.

Mass (m/z) : 173 (M$^+$, 100), 158 (14), 144 (38), 115 (7.5), 104 (11), 77 (4).

Methyl-2-formyl-3-(4-methoxyphenyl)-(Z)-2-propenoate (17)

Mol. F : C$_{12}$H$_{14}$O$_3$.

IR (Neat) : 2951, 2838, 1711, 1630, 1605, 1034, 836 cm$^{-1}$.

$^1$H NMR (200 MHz, CDCl$_3$) : δ 7.7 (s, 1H), 7.4 (d, $J$ = 8.0 Hz, 2H), 6.9 (d, $J$ = 8.0 Hz, 2H), 3.85 (s, 3H), 3.75 (s, 3H), 2.15 (s, 3H).

Mass (m/z) : 206 (100), 195 (41), 146 (97), 103 (41), 91(39), 77 (35).
Section 2. Synthesis of oxime and amino palladacycles and their application in the catalysis of Heck reaction.

**INTRODUCTION AND BACKGROUND**

The transition metal catalyzed C-C bond formation in organic synthesis is very attractive in recent years. The design of structurally important, more selective and active catalysts are attractive prospects in C-C bond forming reactions, for example, synthesis of more active catalysts for Heck reaction. Some of the new, novel and active palladium catalysts for the Heck reaction is described below in detail.

A structurally important N-heterocyclic carbene palladium catalysts were synthesized and applied for the coupling of aryl halides with olefins in homogeneous catalysis as reported by W. A. Herrmann *et al.* as shown in scheme-1.\(^\text{16}\)

Scheme-1
Robin et al. demonstrated the synthesis of extremely highly active orthopalladated triaryphosphite as catalysts in biaryl coupling reactions which gave unprecedented high turnover numbers upto 1000000 and turnover frequencies of nearly 900000 in Suzuki reaction and turnover numbers upto 830000 in the Stille reaction (scheme-2).\(^\text{17}\)

Scheme-2

\[
\begin{align*}
\text{R} \quad \text{X} + \quad \text{R}_1 \quad \text{E} \quad \xrightarrow{\text{catalyst}} \quad \text{R} \quad \text{E} \\
\text{E} = \text{B(OH)}_2 \text{ (suzuki) and } \text{E} = \text{SnR}_3 \text{ (stille)}
\end{align*}
\]

Shaw et al. reported new tri(l-naphthyl)phosphine palladacycles which are very active catalysts for Heck reaction as shown in scheme-3.\(^\text{18}\)
The new cyclopalladated, phosphine free thermally and air stable imine complexes are exceptionally highly active catalysts for the Heck reaction leading to more than million turnover numbers in some cases, reported by M. Ohff et al. as shown in scheme-4.\textsuperscript{19}

Bis-pincer-cyclopalladates containing an ethynediyl or butadiynediyl-bridge, have been used as catalysts for the Heck reaction (scheme-5).\textsuperscript{20}
OBJECTIVE

Our aim was to synthesis structurally important and more stable dimeric palladium complex as a catalyst for the coupling of aryl iodides, bromides and activated chlorides with olefins to achieve high turnover numbers and turnover frequencies. We were also interested in the synthesis of oximepalladacycle, which has a covalent palladium-carbon bond that could stabilize the complex at high temperature and activate aryl chlorides for Heck reaction.

PRESENT WORK

The present work involves designing and synthesizing very active dimeric oxime and amino palladacycles and their application in activating aryl halides including an activated aryl chloride for Heck type coupling reactions. Palladacycles were synthesized according to the
literature method from easily available starting materials like benzaldehyde oxime, benzophenone oxime and $N, N$-dimethylbenzylamine with lithium tetrachloropalladate as shown in scheme-1.\textsuperscript{21}

Scheme-1

\[
\begin{align*}
\text{Scheme-1} \\
\text{R = H, Ph}
\end{align*}
\]

The reactions of various aryl halides, aryl iodide, bromide and an activated aryl chloride with olefins in presence of amino and oximepalladacycle using different co-catalysts $\text{AlCl}_3$, $\text{NBu}_4\text{Br}$ and $\text{ZnCl}_2$ were studied in both small and large scale with 0.001 g of dimeric palladium catalyst to achieve high turn over numbers and turnover frequencies (scheme-2).

Scheme-2

\[
\begin{align*}
\text{Scheme-2} \\
R = \text{OMe, NO}_2, \text{Cl, CN, H} & \quad X = \text{I, Br, Cl}
\end{align*}
\]
Dimeric palladacycles:

1

2, $R = H$

3, $R = Ph$

The results of reactions of various aryl halides with olefins catalyzed by amino and oxime palladacycles are summarized in table-3.
Table-3 : Heck vinylation of aryl halides catalyzed by amine and oxime palladacycle

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Reactant</th>
<th>Olefin</th>
<th>Catalyst</th>
<th>Product</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>TON</th>
<th>TOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>4-Iodoanisole (50 mmol)</td>
<td>Ethylacrylate (100 mol)</td>
<td>1</td>
<td>4-Methoxy Ethyl cinnamate</td>
<td>8</td>
<td>88</td>
<td>89,540</td>
<td>11,190</td>
</tr>
<tr>
<td>2.</td>
<td>4-Iodoanisole (50 mmol)</td>
<td>Styrene (60 mol)</td>
<td>1</td>
<td>4-Methoxy stilbene</td>
<td>48</td>
<td>92</td>
<td>1,38,666</td>
<td>2,888</td>
</tr>
<tr>
<td>3.</td>
<td>Iodobenzene (50 mmol)</td>
<td>Ethyl acrylate (100 mmol)</td>
<td>2</td>
<td>Ethyl cinnamate</td>
<td>7</td>
<td>96</td>
<td>1,45,454</td>
<td>20,778</td>
</tr>
<tr>
<td>4.</td>
<td>Bromobenzene (50 mmol)</td>
<td>Ethylacrylate (100 mmol)</td>
<td>1</td>
<td>ethylcinnamate</td>
<td>34</td>
<td>90</td>
<td>90,000</td>
<td>2,647</td>
</tr>
<tr>
<td>5.</td>
<td>Bromobenzene (50 mmol)</td>
<td>Styrene (60 mmol)</td>
<td>1</td>
<td>stilbene</td>
<td>29</td>
<td>86.6</td>
<td>86,666</td>
<td>2,988</td>
</tr>
<tr>
<td>6.</td>
<td>4-Chloro nitrobenzene (5 mmol)</td>
<td>Ethyl acrylate (10 mmol)</td>
<td>1</td>
<td>4-Nitroethyl cinnamate</td>
<td>31</td>
<td>51</td>
<td>287</td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>4-Chloronitrobenzene (50 mmol)</td>
<td>Styrene (60 mmol)</td>
<td>1</td>
<td>4-Nitrostilbene</td>
<td>42</td>
<td>71</td>
<td>70,000</td>
<td>1,666</td>
</tr>
<tr>
<td>8.</td>
<td>4-Chlorobenzonitrile (5 mmol)</td>
<td>Styrene (6 mmol)</td>
<td>2</td>
<td>4-Cyano stilbene</td>
<td>24</td>
<td>78.5</td>
<td>350</td>
<td></td>
</tr>
<tr>
<td>9.</td>
<td>2-Bromopyridine (5 mmol)</td>
<td>Ethylacrylate (10 mmol)</td>
<td>2</td>
<td>2-Pyridylethyl acrylate</td>
<td>48</td>
<td>68</td>
<td>4,090</td>
<td></td>
</tr>
<tr>
<td>10.</td>
<td>4-Chlorotoluene (2 mmol)</td>
<td>Styrene (4 mmol)</td>
<td>3a</td>
<td>4-Methylstilbene</td>
<td>12</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3b</td>
<td></td>
<td>24</td>
<td>28</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Co-catalyst: \( \text{AlCl}_3 \); temperature 130 °C
Co-catalyst: \( \text{Bu}_4\text{NI} \); Temperature 130 °C
RESULTS AND DISCUSSION

The amino and oxime palladacycles were synthesized and characterized by IR, $^1$H NMR spectra and CHN analysis. The IR spectrum of benzaldehydeoxime palladacycle showed a broad peak at 3370 cm$^{-1}$ and a sharp peak at 1625 cm$^{-1}$ indicating the presence of O-H and C==N groups respectively. The $^1$H NMR spectrum gave a sharp singlet at $\delta$ 8.1 confirming the presence of imine proton and a broad singlet at $\delta$ 9.5 due to the oxime O-H proton. The above IR and $^1$H NMR spectra data were identical with the literature values.28 The IR spectrum of benzophenoneoxime palladacycle showed a sharp peak at 1628 cm$^{-1}$ and a broad peak at 3440 cm$^{-1}$ for C==N and O-H groups correspondingly. The $^1$H NMR spectrum displayed a broad singlet at $\delta$ 9.3 and multiplet at $\delta$ 7.5-7.0 that could be assigned to O-H and aromatic protons accordingly. Further the formation of benzophenoneoxime palladacycle was confirmed by the elemental analysis.

The product obtained from the reaction of $N,N$-dimethylbenzylamine and lithium tetrachloropalladate gave a sharp peak at 2990 cm$^{-1}$ in IR spectrum. In the $^1$H NMR spectrum a sharp singlet appeared at $\delta$ 3.4 is attributed to $N$-CH$_3$ protons where as aromatic protons appeared as multiplet between $\delta$ 7.6-7.3. In addition to these, the elemental analysis also supported the structure of the complex.

The $^1$H NMR spectrum of the product obtained from the reaction of 4-iodoanisole with styrene catalyzed by palladacycle showed a doublet at $\delta$ 6.9 with coupling constant $J = 12.1$ Hz which confirmed the presence of olefinic protons and trans geometry of the product. The mass spectrum showed a molecular ion peak at m/z 210 corresponding to the product. These above data confirmed the structure of one of the product, 1-(4-methoxyphenyl)-2-phenyl-(E)-ethylene.
The IR spectrum of the product obtained from the reaction of aryl iodide with ethyl acrylate showed a sharp peak at 1696-1705 cm\(^{-1}\) indicating the presence of ester carbonyl and another peak at 1600 cm\(^{-1}\) indicating the presence of C=C of \(\alpha, \beta\)-unsaturated ester. The \(^1\text{H}\) NMR spectrum of the product showed two doublets, one at \(\delta 6.3\) with coupling constant \(J = 17.2\) Hz and another at \(\delta 7.6\) with coupling constant \(J = 17.0\) Hz for olefinic protons of the unsaturated esters. The \emph{trans} stereochemistry of the double bond was confirmed based on the coupling constant value (12-18 Hz for \emph{trans} isomer). The mass spectrum of product showed molecular ion peaks supporting the expected products.

The IR spectrum of the product from the reaction of 4-chlorobenzonitrile with styrene showed sharp peak at 2225 cm\(^{-1}\) (C=N) and 1600 cm\(^{-1}\) (C=C). \(^1\text{H}\) NMR spectrum of the product displayed a doublet at \(\delta 7.65\) with coupling constant, \(J = 8.0\) Hz assigned for the aromatic protons of \(A_2B_2\) type and a multiplet at \(\delta 7.55 - 7.50\) indicating the presence of aromatic protons (4H) and another multiplet at \(\delta 7.45-7.50\) due to other aromatic protons (4H). The mass spectrum showed a molecular ion peak at (m/z) 204 for the expected product. The above data confirmed the structure of 1-(4-cyanophenyl)-2-phenyl-(\(E\))-ethylene (25). Similarly, the other cinnamates and stilbenes were characterized by the usual spectroscopic methods.

The reaction of \(p\)-chloronitrobenzene with styrene gave the corresponding nitro substituted stilbene which was confirmed by IR and \(^1\text{H}\) NMR spectral data. The IR spectrum showed a sharp peak at 1604 cm\(^{-1}\) due to the presence of C=C group. In the \(^1\text{H}\) NMR spectrum, a multiplet at \(\delta 7.6 - 7.2\) is assigned to aromatic protons and a doublet at \(\delta 8.3\) with \(J = 16.2\) Hz confirmed the presence of olefinic protons and their \emph{trans} stereochemistry. Similarly, the product of \(p\)-chloronitrobenzene with ethyl acrylate was also characterized. Two sharp peaks at 1714 cm\(^{-1}\) and 1645 cm\(^{-1}\) are due to the presence of carbonyl and C=C groups respectively. The \(^1\text{H}\) NMR spectrum showed two doublets, one at \(\delta 7.7\) (\(J = 14.8\) Hz) and another at \(\delta 6.6\) (\(J = 14.0\))
Hz) which supporting the presence of olefinic protons. Two aromatic protons \( A_2B_2 \) type appeared as a doublet at \( \delta 8.3 \) with coupling constant \( J = 7.5 \) Hz and other two protons appeared as a doublet at \( \delta 7.2 \) Hz with coupling constant \( J = 7.5 \) Hz. The mass spectrum showed a molecular ion peak. The above data confirmed the product (23).

The product formed from the reaction of 2-bromopyridine with ethyl acrylate showed sharp peaks at 1705 cm\(^{-1}\) and 1620 cm\(^{-1}\) for C=O and C=C groups. The \(^1\)H NMR spectrum showed two doublets at \( \delta 7.55 \) \( (J = 17.0 \) Hz) and \( \delta 6.8 \) \( (J = 17.0 \) Hz) confirming the presence of olefinic protons of \( \alpha, \beta \)-unsaturated ester. The above data confirmed the structure of product (26).

**CONCLUSION**

Highly stable dimeric amino and oxime palladacycles were found to be efficient catalyst for Heck reaction. Both aryl bromides and an activated aryl chloride could be reacted with olefins to give high turnover numbers and turnover frequencies.
EXPERIMENTAL

Preparation of Benzaldehydeoxime and Benzophenoneoxime

The oximes required for the synthesis of palladacycle catalysts were prepared based on the literature methods (from the reaction of corresponding aldehyde and ketone with hydroxylamine hydrochloride). The aryl iodides were prepared according to the literature methods from the corresponding amino compounds.

Synthesis of [di-μ-chlorobis(benzophenoneoxime-6-C,N)dipalladium (II) (18)]

A 50 mL RB flask was equipped with magnetic stirring bar and argon balloon charged with a mixture of palladium chloride (0.885 g, 5 mmol) and lithium chloride (0.43 g, 10 mmol) in dry methanol (10 mL) and the reaction was allowed to stir for 1 h at room temperature. After 1 h, a solution of a mixture of benzophenoneoxime (0.98 g, 5 mmol) and sodium acetate (0.41 g, 5 mmol) in dry methanol (5 mL) was added slowly with stirring. The reaction was allowed to stand for a day and then diluted with distilled water (200 mL); the yellow solid formed was filtered and dried.

M.P : 180 °C.

IR (Nujol) : 3280, 3200, 1629, 1338, 1039, 1024 cm⁻¹.

¹H NMR (200 MHz, CDCl₃) : δ 8.5 - 8.2 (bm, 2H), 7.6 - 6.4 (m, 18H).

Analysis

Calculated : C (46.18), H (2.98), N (4.14)

Found : C (46.29, H (2.90), N (4.11).

Synthesis of [di-μ-chlorobis(benzaldehydeoxime-6-C,N)dipalladium (II) (19)]

A mixture of lithium chloride (0.43 g, 10 mmol) and palladium chloride (0.885 g, 5 mmol) was charged into a 25 mL RB flask equipped with magnetic stirring bar and it was allowed to heat at 100 °C for 45 minutes, the reaction mixture under distillation at reduced
pressure at 5 mm gave dry solid, to this dry methanol (15mL) was added, followed by addition of
a mixture of benzaldehyde oxime (0.785 g, 5 mmol) and sodium acetate (0.41 g, 5 mmol) in dry
methanol (5 mL). The reaction mixture was allowed to stand for 1 day and diluted with distilled
water (200 mL), yellow crystals formed, filtered and dried.

**Yield**

: 1.56 (60 %)

**M. P**

: 200 °C

**IR (Nujol)**

: 3410, 1622, 1595, 1189 cm⁻¹

**¹H NMR (200 MHz, CDCl₃)**:  δ 9.65 (s, 2H), 8.05 (s, 2H) 7.9 - 7.8 (m, 2H), 7.5 - 7.3 (m, 4H)

**Synthesis of [di-µ-chlorobis(dimethylbenzylamine-6-C,N)dipalladium (II)]**³³

A 50 mL RB flask was equipped with a magnetic stirring bar and argon balloon was
charged with a mixture of PdCl₂ (0.885 g, 5 mmol) and LiCl (0.43 g, 10 mmol) in dry methanol
and the reaction is allowed to stir for 1 hour. After one hour a solution of a mixture of N,N-
dimethylbenzylamine and sodium acetate (0.41 g, 5 mmol) in dry methanol (5 mL) was added
slowly with stirring. The reaction was allowed to stir for a day and then diluted with distilled
water (200 mL). A pale yellow colour precipitate was formed, filtered and dried.

**IR (Nujol)**

: 2932, 1597, 1043, 940, 862 cm⁻¹

**¹H NMR (200 MHz, CDCl₃+ DMSOδ)**: δ 7.21-7.02 (m, 4H), 6.9 - 6.85 (m, 4H), 3.92 (s, 4H),

2.72 (s, 6H)

**General procedure for the Heck reaction catalyzed by Palladacycle.**

**Small scale reaction**

A 25 mL RB flask equipped with magnetic stirring bar, reflux condenser and argon
balloon was charged with aryl iodide / bromide/chloride (5 mmol), olefin (10 mmol), Potassium
carbonate (2.75 g, 10 mmol) and palladacycle catalyst (0.001 g, 0.005 mmol) in N-methyl pyrrolidinone (10 mL). The reaction mixture was allowed stir at 140-150 °C for 4-24 h and neutralized with dil HCl (10% by volume). The product was extracted with ethyl acetate (3 x 5 mL), the combined organic extracts dried over anhydrous sodium sulphate and concentrated under reduced pressure to yield the crude product. The crude product on silica gel column chromatographic purification using pet. ether-ethyl acetate mixture gave the pure products.

Large scale reaction for TON and TOF

A 25 mL RB flask equipped with magnetic stirring bar, reflux condenser and argon balloon was charged with aryl iodide / bromide /chloride (75 mmol), olefin (150 mmol), potassium carbonate (20.7 g, 150 mmol) and palladacycle catalyst (0.001 g, 0.005 mmol) in N-methyl pyrrolidinone (100 mL). The reaction mixture was allowed stir at 140-150° C for 4-24 h and neutralised with dil HCl (10% by volume). The product extracted with ethyl acetate (4 x 50 mL), the combined organic extracts was dried over anhydrous sodium sulphate and concentrated under reduced pressure to yield the crude product. The crude product on silica gel column chromatographic purification using pet.ether-ethyl acetate mixture gave the pure products.

Ethyl 3-(4-methoxyphenyl)-(E)-2-propenoate (20)

Mol. F : \( \text{C}_12\text{H}_{14}\text{O}_3 \).

IR (Neat) : 2985, 1710, 1600, 1510, 1240, 1040, 830 cm\(^{-1}\).

\( ^1H \) NMR (200 MHz, CDCl\(_3\)) : 8 7.6 (d, \( J = 17.0 \) Hz, 1H), 7.5 (d, \( J = 8.5 \) Hz, 2H), 6.9 (d, \( J = 8.5 \) Hz, 2H), 6.3 (d, \( J = 17.0 \) Hz, 1H), 4.2 (q, \( J = 8.0 \) Hz, 2H), 3.8 (s, 3H), 1.3 (t, \( J = 8.0 \) Hz, 3H).

\( ^13C \) NMR (50.35 MHz, CDCl\(_3\)) : 166.9, 161.2, 143.7, 129.5, 127.0, 115.60, 114.11, 60.00,
Mass (m/z) : 206 (100), 191 (1), 178 (6), 161 (19), 154 (30), 135 (9), 126 (20), 98 (63).

4-Methoxy stilbene (21)

Mol. F : C_{13}H_{14}O

M. P : 135 °C

IR (CHCl_{3}) : 2923, 1599, 1375, 1251, 814 cm\(^{-1}\).

\(^1H\) NMR (200 MHz, CDCl_{3}) : 7.6 - 7.25 (m, 7H), 7.1 (d, J = 8.0 Hz, 2H), 6.9 (d, J = 12.1 Hz, 1H), 3.85 (s, 3H).

Mass (m/z) : 210 (M\(^+\), 100), 195 (25), 179 (17), 165 (66), 152 (59), 115 (26), 105 (25), 91(41), 77 (29).

Ethyl-3-phenyl-(E)-2-propenoate (22)

Mol. F : C_{11}H_{12}O_{2}

IR (Neat) : 2980, 1716, 1638, 1592, 1490, 1269, 1173, 883 cm\(^{-1}\).

\(^1H\) NMR (200 MHz, CDCl_{3}) : 5 7.7 (d, J = 8.0 Hz, 1H), 7.6 - 7.5 (m, 2H), 7.4 - 7.25 (m, 3H),

1.45 (d, J = 16.0 Hz, 1H), 4.25 (q, J = 8.0 Hz, 2H), 1.35(t, J = 8 Hz, 3H).

Mass (m/z) : 180 (M\(^+\), 100), 104 (42), 77 (100).

1, 2-Diphenyl-(E)-ethylene (22a)

Mol. F : C_{14}H_{12}

M. P : 120 °C

IR (Nujol) : 2855, 1602, 1506, 1375, 920, 765 cm\(^{-1}\).

\(^1H\) NMR (200 MHz, CDCl_{3}) : 8 \text{ 7.6 (d, } J = 14.0 \text{ Hz, 2H), 7.45 -7.25 (m, 10H)}

Mass (m/z) : 180 (M\(^+\), 100), 104 (42), 77 (100).
Ethyl-3-(4-nitrophenyl)-(E)-2-propenoate (23)

Mol. F : \( \text{C}_{12}\text{H}_1\text{NO}_4 \).

M. P : 62 °C

IR (Nujol) : 2925, 2854, 1714, 1645, 1109, 1029, 960 cm\(^{-1} \).

\(^1\)H NMR (200 MHz, CDCl\(_3\)) : \( \delta \) 8.3 (d, \( J = 7.5 \) Hz, 2H), 7.7 (d, \( J = 14.8 \) Hz, 1H), 7.2 (d, \( J = 7.5 \) Hz, 2H), 6.6 (d, \( J = 14.8 \) Hz, 1H), 4.2 (q, \( J = 7.0 \) Hz, 2H), 1.3 (t, \( J = 7.0 \) Hz, 3H).

Mass (m/z) : 233 (M\(^+\), 5), 188 (43), 144 (61), 76 (100).

1-(4-nitrophenyl)-2-phenyl-(E)-ethylene (24)

Mol. F : \( \text{C}_{14}\text{H}_1\text{NO}_2 \).

M. P : 96 °C

IR (Nujol) : 1604, 1034, 850, 765 cm\(^{-1} \).

\(^1\)H NMR (200 MHz, CDCl\(_3\)) : \( \delta \) 8.3 (d, \( J = 16.2 \) Hz, 2H), 7.6 - 7.2 (m, 9H).

Mass (m/z) : 225 (M\(^+\), 69), 178 (100), 151 (15), 165 (11), 77 (8).

1-(4-cyanophenyl)-2-phenyl-(E)-ethylene (25)

Mol. F : \( \text{C}_{15}\text{H}_1\text{N} \).

M. P : 103 °C

IR (Nujol) : 2854, 2225, 1600, 1504, 1377, 922, 768 cm\(^{-1} \).

\(^1\)H NMR (200 MHz, CDCl\(_3\)) : \( \delta \) 7.65 (d, \( J = 8.0 \) Hz, 2H), 7.55 - 7.50 (m, 4H), 7.45 - 7.25 (m, 4H), 7.2 (d, \( J = 14.0 \) Hz, 1H).

Mass (m/z) : 204 (16), 190 (49), 177 (20), 165 (19), 151(11), 127 (8), 113 (6), 102 (41), 76 (59).
Ethyl- 3-(2-pyridyl)-(E)-2-propenoate (26)

Mol. F  
: C_{10}H_{12}NO_{2}.

IR (Neat)  
: 2983, 2854, 1705, 1620, 1043, 944, 776 cm^{-1}.

$^{1}H$ NMR (200 MHz, CDCl$_{3}$)  
: $\delta$ 8.55 - 8.50 (m, 1H), 7.6 (m, 1H), 7.55 (d, $J$=17.0 Hz, 1H), 7.3 (d, $J$= 6.0 Hz, 1H), 7.2-7.1 (m, 1H), 6.8 (d, $J$=17.0 Hz 1H), 4.2 (q, $J$= 7.4Hz, 2H), 1.34 (t, $J$ = 7.5 Hz, 3H)

$^{13}$C NMR (50.35 MHz, CDCl$_{3}$): $\delta$ 166.78, 153.20, 150.30, 143.47, 136.90, 124.34, 124.23, 122.66, 60.72, 14.42.
References


Spectra
1H NMR and 13C NMR Spectra of 16

![Chemical Structure](image-url)