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Tetrahedron
Tetrahedron 60 (2004) 2163–2172

# Mizoroki–Heck reaction, catalysis by nitrogen ligand Pd complexes and activation of aryl bromides☆

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Received 26 September 2003; revised 10 November 2003; accepted 4 December 2003

**Abstract**—Nitrogen ligands are an excellent alternative for the traditional P-ligands in the Pd catalyzed Mizoroki–Heck reaction. Pd complexes of dimethyl glyoxime, 8-hydroxyquinoline, salen, picolinic acid, DAB ligands gave high yields of the *E*-cinnamates and *E*-stilbenes. Acetophenone oxime *N*,*N*-dimethybenzyl amine and ferrocenyl oxime palladacycle were better catalysts and comparable yields, TON (95,000) and TOF's (2500 $h^{-1}$) to P-ligand catalysts, were obtained. Aryl iodides, aryl bromides and in a few cases, aryl chlorides could be also be activated by these complexes by the use of Lewis acid and $(C_4H_9)_4NI$ as additive. DAB ligands gave good yields with electron rich aryl bromides and the use of ionic liquid improved the yield. These metal complexes can be readily synthesized and the N-ligands possess the advantage of easy functional group modifications and convenient synthetic methods compared to P-ligands. The degradation reactions associated with P-ligands is not observed in the N-ligands, with comparable high thermal, moisture and air stability and insensitivity.


## 1. Introduction

Nitrogen compounds are commonly used ligand in transition metal chemistry and equal in number and reactions to P-ligands.[1] Palladium complexes with various phosphines as ligands have been most commonly used as catalysts for the Mizoroki–Heck reaction.

Cyclopalladated tris-*o*-tolylphosphine, *N*-heterocyclic carbene, tridentate aryl bisphosphine Pd (II) (PCP), triaryl phosphites, are excellent catalysts giving high yields, TON and TOF for the Mizoroki–Heck reaction.[2] A major drawback of the use of phosphine ligands in such catalytic reactions is the oxidation of the phosphine to a phosphine oxide as well as cleavage of the P–C bond, causing degradation of the ligand, reduction of the metal and termination of the catalytic cycle.[3] Cyclopalladated aromatic rings are the choice systems for such catalysts due to the high thermal, moisture and oxidative stability. A variety of novel C–N, C–S palladacycles incorporating NHC,[4] imine,[5] thioether [6] and oxime[7] have been reported with high turnover numbers upto $10^5$–$10^6$. These palladacycles are thermally stable and insensitive to moisture and air. Several novel Ni, Cu, Co, Ir, Rh, Pt catalysts have also been reported for the Mizoroki–Heck reaction.[8]

Nitrogen based ligands like DMG, 8-hydroxyquinoline, salen, picolinic acid, tmeda and their metal complexes and palladacycles from substituted *N*,*N*-dimethylbenzylamine, benzaldoxime and benzophenone oxime can be easily synthesized from readily available precursors by a variety of convenient synthetic methods.[9] Such ligands are not as readily oxidizable as phosphines and the metal complexes with a covalently bonded Pd to the aromatic ring, could be more stable and efficient catalysts (Scheme 1) and activate unreactive bromides and chlorides.[10] The various ligands also offer scope for electronic tuning by easy functionalization to influence the reaction in the desired direction including asymmetric induction.[11]

## 2. Results and discussion

Reaction of DMG, DAB, 8-hydroxyquinoline, salen and picolinic acid with $PdCl_2$ by well established procedures gives the corresponding Pd (II) complexes in high yield (Scheme 1).[6,12] In all these complexes, the metal is in the +2 oxidation state. The DAB ligands are readily prepared by the condensation of various amines with glyoxal and 2,3-butanedione (compared with the tedious synthesis of phosphines). The strong σ-donor and π-acceptor properties of the DAB makes them excellent ligand for the activation of the less reactive aryl bromides and chlorides. Salen and

☆ NCL Communication No.: 6654.

*Keywords*: Nitrogen ligands; Oxime palladacycles; Amine palladacycles; Dimethyl glyoxime; Ferrocenyl oxime palladacycle; Picolinic acid; Lewis acid; 8-Hydroxyquinoline.

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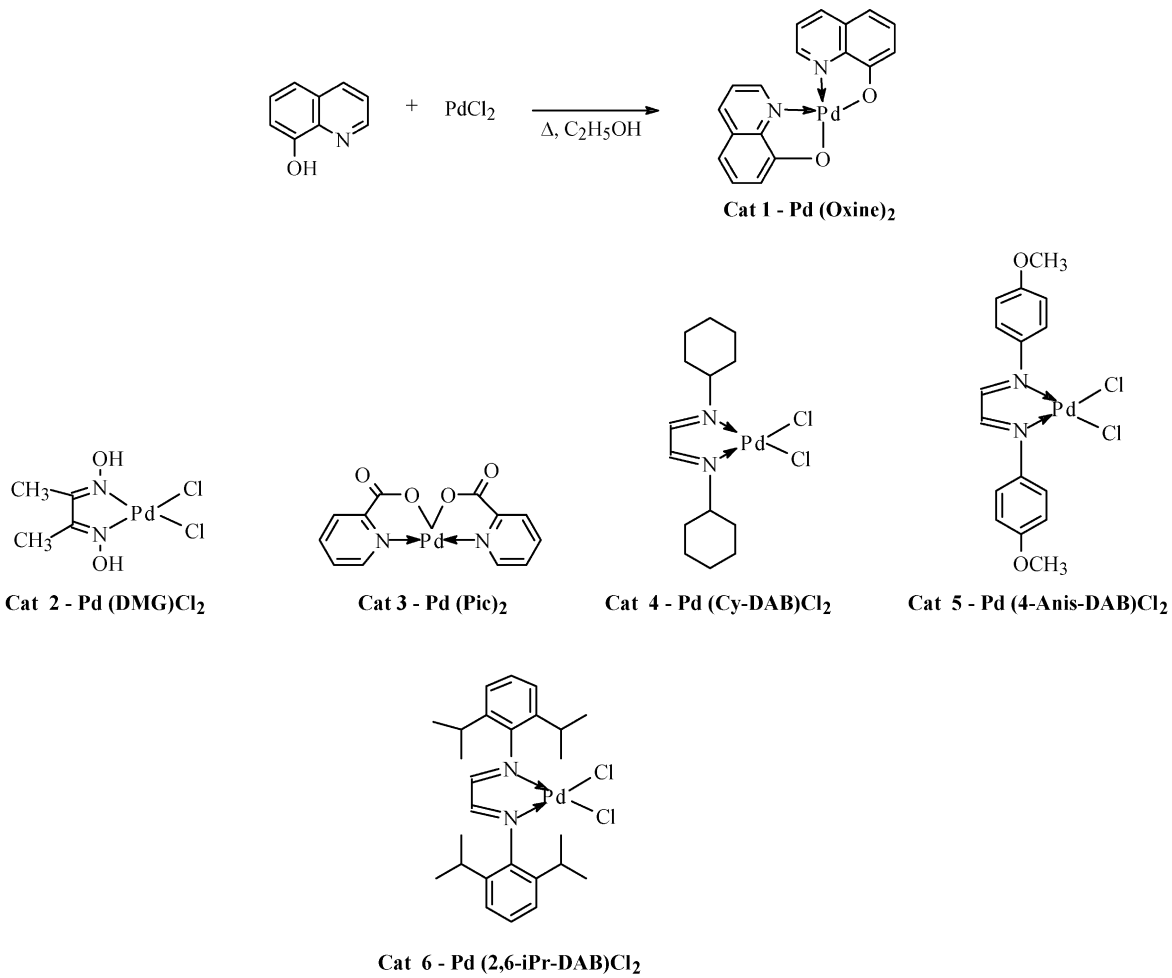
0040–4020/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2003.12.012

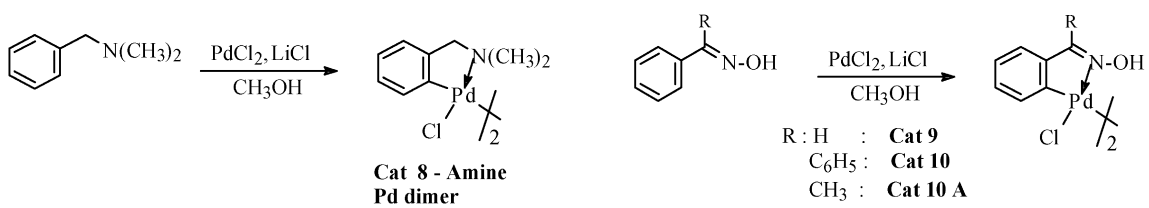



**Scheme 1.** Preparation of dimethylglyoxime, 8-hydroxyquinoline, diimine palladium complexes.

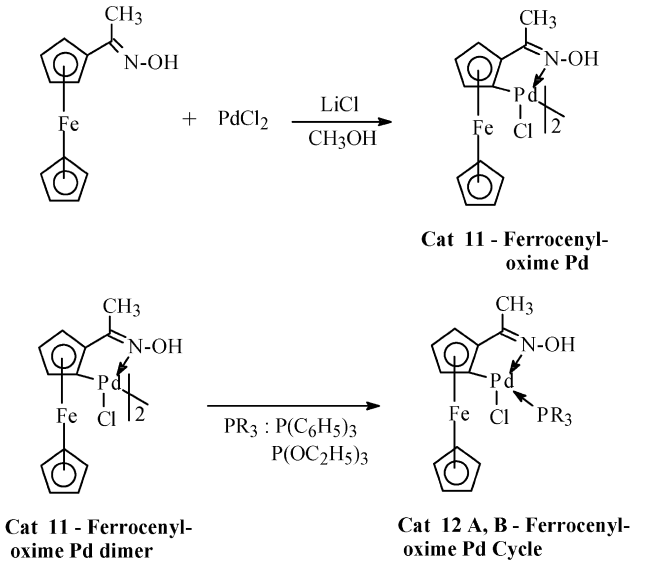
picolinic acid with the −COOH and −OH bonding to Pd, offer different electronic properties to these catalysts.

Cyclopalladation of benzaldehyde oxime, acetophenone oxime, benzophenone oxime, *N*,*N*-dimethyl benzyl amine and acetylferrocenyl oxime is facile and carried out according to the reported literature procedure to give the dimeric palladacycles (Scheme 2).[9] Ferrocene is an electron rich aromatic metal complex and has interesting properties due to its sandwich nature. The electron rich ferrocene is also expected to increase the electron density on the Pd enabling activation of less reactive aryl halides. Monomeric complexes of the dimeric palladacycles were prepared for studying the ligand effect by complexation to $P(C_6H_5)_3$, $P(OC_2H_5)_3$ and saturated *N*-heterocyclic carbenes (Scheme 3).[13] *N*-heterocyclic carbene orthopalladated oxime and amine catalysts were prepared by the refluxing of the corresponding dimeric palladacycles with the saturated *N*-heterocyclic carbene dimers in *m*-xylene in moderate yield. The ferrocene ring and the *N*-heterocyclic carbenes impart greater air, moisture and thermal stability to the palladacycles as well as its activity (Scheme 4).[14]

The Mizoroki–Heck reaction of 4-iodo anisole and 4-chloro iodo benzene with ethyl acrylate and styrene was catalyzed by these Pd complexes (**Cat 1**–**7**) to form the *E*-ethyl cinnamates (**18**, **19**) and *E*-stilbenes (**25**, **36**) in high yields (85–95%, Table 1).[16a,b,j,18] Bromo benzene and 4-bromo phenol could also be activated by these complexes under the reaction conditions studied to give moderate yields of the substituted products (8–48%).[17b,c] As a comparison, other catalysts like $MnO_2$, Ni, Mn and Cu salen (**Cat**-**17A**,**B**,**C**) complexes were the least active (21–60% yield), requiring high temperatures for the reaction.[17] The heterogeneous Ni/$Al_2O_3$ gave a 95% yield of *E*-4-methoxy ethyl cinnamate (**18**) in 2 h. $PdCl_2\{P(C_6H_5)_3\}_2$ in conjunction with $ZnCl_2$ or




**Scheme 2.** Preparation of amine and oxime palladacycles.

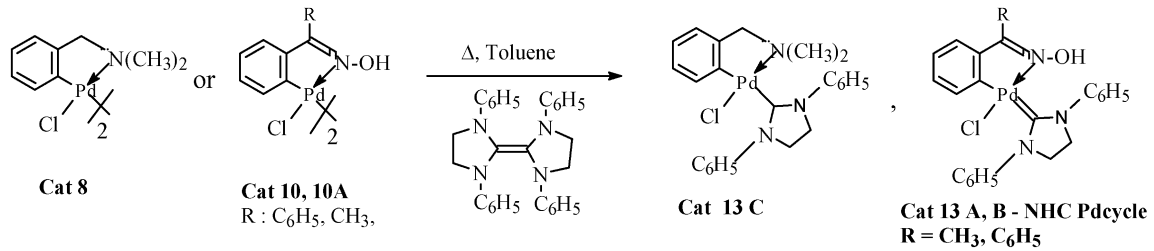



**Scheme 3.** Preparation of ferrocenyl oxime palladacycle.

PVP (polymeric base) gave yields of 40–90%. Tetrabutyl ammonium bromide and iodide as additives activated 2-chloro pyridine to give the 2-pyridyl ethyl acrylate (**24**)[16f,18] catalyzed by $Pd(OCOCH_3)_2$ (40% yield) and benzophenone oxime palladacycle dimer (60% yield). No reaction with aryl bromides was observed in presence of the salen catalysts.

The reaction of bromobenzene with ethyl acrylate was catalyzed by $PdCl_2$ (cyclohexyl-DAB) (**Cat-4**) to give the *E*-ethyl cinnamate in 63% yield. $K_2CO_3$ was the base of choice and *N*-methylpyrrolidinone was used as solvent. With the same catalyst, reaction of bromobenzene with styrene gave the *E*-stilbene in 64% yield. 4-Bromophenol and 4-*N*,*N*-dimethyl amino bromobenzene gave only 45 and 46% yield of the substituted ethyl cinnamate (**28**, **29**),[16j,k,18] while 1-bromonaphthalene gave 43% yield (**26**).[16h,18] With styrene, 1-bromonaphthalene and 4-bromophenol gave 89% (**27**)[16i] and 64% (**28**)[16j] yield of the substituted products while 4-*N*,*N*-dimethylamino bromobenzene gave only 10% yield (**30**).[16l,18] Rate acceleration was observed in the reaction of 1-bromonaphthalene with styrene and reaction was complete in 45 min, compared to the long reaction times for other substrates and catalysts. No reaction was observed with 4-chlorotoluene and 4-chloronitrobenzene.

Use of other DAB ligands (**Cat-5**, *p*-anisidine DAB, **Cat-6**, 2,6-diisopropylaniline DAB and **Cat-7**, *p*-anisidine-dimethyl DAB) gave only moderate yields of the substituted products with different aryl bromides. In all these reactions




**Scheme 4.** Preparation of saturated *N*-heterocyclic carbene palladacycles.

**Table 1**. DMG, 8-hydroxyquinoline, salen, picolinic acid Pd complexes catalyzed reaction of aryl halides

| S. No. | Aryl halide | Cocatalyst/base | Olefin | Catalyst | Time (h) | Yield (%) |
|---|---|---|---|---|---|---|
| 1 | 4-$CH_3O$·$C_6H_4$·I | — | $C_5H_8O_2$[a] | **1**–Pd $(C_9H_6NO)_2$ | 30 | 90 |
| | | | | **2**–Pd $(DMG)Cl_2$ | 6 | 80 |
| | | | | **3**–Pd $(2\text{-}COOH.C_5H_4N)_2$ | 8 | 89 |
| 2 | 4-Cl·$C_6H_4$·I | — | $C_5H_8O_2$ | **1**–Pd $(C_9H_6NO)_2$ | 24 | 69 |
| | | | | **2**–Pd $(DMG)Cl_2$ | 8 | 68 |
| | | | | **3**–Pd $(2\text{-}COOH.C_5H_4N)_2$ | 24 | 84 |
| 3 | $C_6H_5$·Br | — | $C_5H_8O_2$ | **1**–Pd $(C_9H_6NO)_2$ | 24 | 48 |
| | | | | **2**–Pd $(DMG)Cl_2$ | 24 | 48 |
| | | | | **3**–Pd $(2\text{-}COOH.C_5H_4N)_2$ | 24 | 57 |
| 4 | 4-HO·$C_6H_4$·Br | — | $C_8H_8$[b] | **1**–Pd $(C_9H_6NO)_2$ | 24 | NR |
| | | | | **2**–Pd $(DMG)Cl_2$ | 24 | 16 |
| | | | | **3**–Pd $(2\text{-}COOH.C_5H_4N)_2$ | 24 | 8 |
| 5 | 4-$CH_3O$·$C_6H_4$·I | — | $C_8H_8$ | **17A**-Ni $(C_{16}H_{14}N_2O_2)$ | 24 | 42 |
| 6 | 4-$CH_3O$·$C_6H_4$·I | — | $C_8H_8$ | **17B**-Mn $(C_{16}H_{14}N_2O_2)$ | 24 | 21 |
| 7 | 4-$CH_3O$·$C_6H_4$·I | — | $C_5H_8O_2$ | **17C**-Cu $(C_{16}H_{14}N_2O_2)$ | 24 | 60 |
| 8 | 4-$CH_3O$·$C_6H_4$·I | — | $C_5H_8O_2$ | $MnO_2$ | 24 | 80 |
| 10 | 4-$CH_3O$·$C_6H_4$·I | PVP[c] | $C_5H_8O_2$ | $PdCl_2\{P(C_6H_5)_3\}_2$ | 12 | 90 |
| 11 | 4-$NO_2$·$C_6H_4$·I | $ZnCl_2$ | $C_5H_8O_2$ | $PdCl_2\{P(C_6H_5)_3\}_2$ | 18 | 40 |
| 12 | 2-Cl·$C_5H_4N$ | $(C_4H_9)_4NI$ | $C_5H_8O_2$ | **9**$\{PdC_{13}H_{10}ClNO\}_2$[d] | 24 | 60 |
| 13 | 2-Cl·$C_5H_4N$ | $(C_4H_9)_4NBr$ | $C_5H_8O_2$ | $Pd(OCOCH_3)_2$ | 4 | 50 |
| 14 | 4-$CH_3O$·$C_6H_4$·I | — | $C_5H_8O_2$ | $Ni/Al_2O_3$ | 2 | 95 |

[a] $C_5H_8O_2$, ethyl acrylate.
[b] $C_8H_8$, styrene; NR, no reaction.
[c] PVP, polyvinylpyridine.
[d] $\{PdC_{13}H_{10}ClNO\}_2$, di-μ-chlorobis (benzophenoneoxime-6-C,N) dipalladium.

**Table 2**. $PdCl_2$(DAB) catalyzed reaction of aryl bromides

| S. No. | Aryl bromide | Olefin | Catalyst | Time (h) | Yield (%)[a] | TON (TOF) |
|---|---|---|---|---|---|---|
| 1 | $C_6H_5Br$ (2 mmol) | $C_5H_8O_2$[b] | **4** | 24 | 63 | 63 |
| | | | **5** | 45 | 16 | 16 |
| | | | **6** | 20 | 32 | 32 |
| | | | **7** | 24 | 40 | 40 |
| 2 | $C_6H_5Br$ (10 mmol) | $C_7H_{12}O_2$ | **4** | 24 | 20 | 2666 (111)[c] |
| 3 | $C_6H_5Br$ (10 mmol) | $C_7H_{12}O_2$ | **4A** | 24 | 26.5 | 132[d] (5) |
| 4 | $C_6H_5Br$ (50 mmol) | $C_8H_8$[e] (50 mmol) | **4** | 24 | 64 | 64 |
| | | | **4A** | 48 | 15 | 37,600 (783)[f] |
| | | | **5** | 24 | 21 | 21 |
| | | | **6** | 29 | 31 | 31 |
| | | | **7** | 24 | 19 | 19 |
| 5 | 1-$C_{10}H_7Br$ | $C_5H_8O_2$ | **4** | 24 | 45 | 45 |
| | | | **5** | 24 | 30 | 30 |
| | | | **6** | 24 | 44 | 44 |
| | | | **7** | — | — | — |
| 6 | 1-$C_{10}H_7Br$ | $C_8H_8$ | **4** | 45 mins | 89 | 89 |
| | | | **5** | 31 | 44 | 44 |
| | | | **6** | 24 | 78 | 78 |
| | | | **7** | 24 | 22 | 22 |
| 7 | 11-$C_{10}H_7Br$ (10 mmol) | $C_8H_8$ | **4** | 3 | 86 | 17,200 (5733)[g] |
| 8 | 11-$C_{10}H_7Br$ (10 mmol) | $C_8H_8$ | 4A | 6 | 76 | 380 (63)[h] |
| 9 | 4-HO·$C_6H_4$·Br | $C_5H_8O_2$ | **4** | 24 | 45 | 45 |
| | | | **5** | 42 | nr | — |
| | | | **6** | 24 | nr | — |
| | | | **7** | 24 | 8 | 8 |
| 10 | 4-HO·$C_6H_4$·Br | $C_8H_8$ | **4** | 24 | 64 | 64 |
| | | | **5** | 24 | nr | — |
| | | | **6** | 24 | 38 | 38 |
| | | | **7** | 24 | nr | — |
| 11 | 4-$(CH_3)_2$N·$C_6H_4$·Br | $C_5H_8O_2$ | **4** | 24 | 46 | 46 |
| | | | **5** | 48 | nr | — |
| | | | **6** | 24 | 25 | 25 |
| | | | **7** | 24 | nr | — |
| 12 | 4-$(CH_3)_2$N·$C_6H_4$·Br | $C_8H_8$ | **4** | 24 | 10 | 10 |
| | | | **5** | 24 | nr | — |
| | | | **6** | 24 | nr | — |
| | | | **7** | 24 | nr | |

[a] Reaction conditions: halide: olefin: base: **Cat-2**: 4: 4: 0.02—temp.: 150 °C.
[b] ($C_5H_8O_2$, Ethyl acrylate.
[c] Reaction conditions: halide: olefin: base: TBAB: **Cat-4**: 10: 10: 15: 1: 0.00075—temp.: 140 °C.
[d] Reaction conditions: halide: olefin: base: **Cat-4A**: Cy-DAB—10: 10: 15: 0.02: 0.04—temp.: 140 °C.
[e] $C_8H_8$, Styrene (i) nr, no reaction.
[f] Reaction conditions: halide: olefin: base: **Cat-4A**: **Cy-DAB**: 50: 50: 55: 0.0002: 0.0004—temp.: 140 °C.
[g] Reaction conditions: halide: olefin: base: TBAB: **Cat-4**: 10: 10: 15: 1: 0.0005—temp.: 120 °C.
[h] Reaction conditions: halide: olefin: base: **Cat-4A**: Cy-DAB—10: 10: 15: 0.02: 0.04—temp.: 120 °C; solvent-NMP (6–12 ml); **Catalyst-4**,**5**,**6**,**7**—see Scheme 1.

**Table 3**. $PdCl_2$ (DAB) catalyzed reaction of aryl halides in ionic liquid

| S. No. | Aryl bromide | Olefin | Catalyst | Time (h) | Yield (%) |
|---|---|---|---|---|---|
| 1 | $C_6H_5Br$ | $C_7H_{12}O_2$[a] | **4** | 24 | 70 |
| | | $C_7H_{12}O_2$ | **5** | 24 | 68 |
| | | $C_5H_8O_2$ | **6** | 20 | 67 |
| | | $C_7H_{12}O_2$ | **7** | 24 | 45 |
| 2 | $C_6H_5Br$ | $C_8H_8$[b] | **5** | 24 | 57 |
| | $C_6H_5Br$ | $C_8H_8$ | **7** | 24 | 35 |
| 3 | 4-HO·$C_6H_4$·Br | $C_5H_8O_2$ | **4** | 24 | 46 |
| 4 | 1-$C_{10}H_7Br$ | $C_5H_8O_2$ | **4** | 24 | 67 |
| | | | **5** | 24 | 50 |
| | | | **6** | 24 | 85 |
| 5 | 1-$C_{10}H_7Br$ | $C_8H_8$ | **5** | 31 | 87 |
| | | | **7** | 24 | 55 |
| 6 | 4-$(CH_3)_2$N·$C_6H_4$·Br | $C_8H_8$ | **5** | 48 | 52 |
| | | | **6** | 24 | 57 |

Reaction conditions: A: ArBr (3 mmol), butylacrylate (3 mmol), $Na_2CO_3$ (6 mmol), $HCOONH_4$ (0.1 mmol), $(C_4H_9)_4NBr$ (6 mmol); temperature: 130 °C; B: ArBr (2 mmol), styrene (5 mmol), HCOONa (0.147 mmol), $CH_3COONa$ (2.4 mmol), $(C_4H_9)_4NBr$ (6 mmol), temperature: 130 °C.
[a] $C_5H_8O_2$, ethyl acrylate.
[b] $C_8H_8$, styrene.

Pd is in the +2 oxidation state. For comparison, Pd $(dba)_2$ (**4A**–Pd-0) as catalyst with Cy-DAB as ligand gave comparable yields to $PdCl_2$(DAB) with bromobenzene and butyl acrylate (**34**, 26.5%, TON- 132, TOF- 5 $h^{-1}$)[16o] and bromonaphthalene and styrene (76%, TON- 380, TOF, 63 $h^{-1}$). Reaction of bromobenzene (50 mmol) with styrene gave 1.354 g stilbene (15%, TON- 37, 600; TOF- 783 $h^{-1}$).

These results are comparable to or better than the results obtained with $PdCl_2\{P(C_6H_5)_3\}_2$ as catalyst (20–30% yield) under similar conditions for the same aryl bromides. These results are comparable to the yields obtained with the DMG, picolinic acid and 8-hydroxy quinoline ligands for bromobenzene.

The diimine from the condensation of benzaldehyde and ethylenediamine was also used to prepare a Pd complex. However, the use of this catalyst also gave only moderate yields (24–55%) in the reactions of bromo benzene and bromo naphthalene with ethyl acrylate. The use of

$(C_4H_9)_4NBr$ as ionic liquid-solvent with Pd benzothiazole carbene complex as catalyst has been shown to improve the reactivity and yield in the Mizoroki–Heck reaction.[14,15]The reaction of bromobenzene and bromonaphthalene with ethyl acrylate in $(C_4H_9)_4NBr$ as ionic liquid solvent, catalyzed by $PdCl_2$(Cy-DAB) **Cat-4** gave higher yields (70 and 66%) of the substituted product while the other catalysts **5**, **6** and **7** gave moderate to high yields of the substituted product (52–87%) (Table 3) compared to the reactions in NMP (Table 2).

Orthometallated aryl oxime, amine palladacycles (**Cat 8–10**,**10A**) catalyze the reaction (Table 4) of aryl iodides, bromides and electron deficient chlorides with ethyl acrylate and styrene to give high yields of the substituted products (*E*-cinnamate and *E*-stilbene) with high turn over numbers (72,000–145,454) and TOF's (1625–20,780). The bromides and chlorides take longer reaction times for complete conversion.

Electron withdrawing groups activate aryl chlorides. The use of a Lewis acid ($ZnCl_2$), as a co-catalyst which would help labilize the halide, increased the reaction rate and the yield of the reaction. The reaction of bromobenzene with ethyl acrylate and styrene was catalyzed by the palladacycle **10** giving 90 and 96% yields of *E*-ethyl cinnamate and *E*-stilbene (TON- 450) in 1 h (shorter reaction time compared to the other catalysts). The TON for bromobenzene with the catalyst **8** (87,000-90,000) was higher than with the catalyst **9** (72,000-78,000). When aluminium chloride was used as a co-catalyst, the reaction of 4-chlorotoluene, with styrene, gave the substituted product (**35**, as *E*-isomer) in 18% yield.[16p,18]

$(C_4H_9)_4NI$ was also used as co-catalyst for the reaction of 4-chlorotoluene and 2-chloropyridine with ethyl acrylate and styrene in the presence of palladacycle **10**. The normal substitution products were obtained in moderate yields. Oxime and *N*,*N*-dimethyl benzyl amine palladacycles show high yields, TON's and TOF's in the reaction of aryl iodides and bromides.[1–5] The reaction of 4-iodoanisole and ethyl acrylate or styrene proceeded readily in *N*-methylpyrrolidinone as solvent and catalyzed by ferrocenyl palladacycle **11**, to give (*E*)-4-methoxy ethyl cinnamate and (*E*)-4-methoxystilbene in 74 and 69% yields, respectively.

The monomeric catalysts **12A** and **12B** gave a 93% yield of (*E*)-4-methoxy ethyl cinnamate and 73 and 67% yields of (*E*)-4-methoxystilbene. The reaction of of 4-iodoanisole (25 mmol) with ethyl acrylate (50 mmol) in the presence of $2.6\times10^{-4}$ mmol of catalyst **11**, gave the (*E*)-4-methoxy ethyl cinnamate in 65% yield with a turnover number of 62,500. Increasing the catalyst concentration to $1.3\times10^{-3}$ led to shorter reaction time, but did not improve the yield (76–84%). The catalysts **12A** and **12B** gave 84 and 92% yields of (*E*)-4-methoxy ethyl cinnamate (catalyst concentration $1.5\times10^{-3}$ mmol).

Monomeric complexes **11**, **12A** and **12B** showed appreciable catalytic activity for the reaction of relatively inactive bromobenzene with ethyl acrylate and stilbene to afford 77–85% yields of (*E*)-ethyl cinnamate and (*E*)-stilbene (TON's 5266–15,192). The reaction of 1-bromonaphthalene with both ethyl acrylate and styrene gave ethyl (*E*)-3-(1-naphthyl) propenoate and (*E*)-2-phenyl-1-(1-naphthyl) ethene in 83–97% yield (TON's 25,000–36,153). Sodium acetate was a better base than $K_2CO_3$. 4-Bromophenol reacted with ethyl acrylate to give the 4-(*E*)-hydroxy ethyl cinnamate in only 20–45% yields.

Activated aryl chlorides, such as 4-chloro nitrobenzene, 4-chloro acetophenone and 4-chloro benzonitrile also reacted with styrene to give the corresponding *E*-stilbenes in moderate yields (22–53%, **31**, **32**, **33**).[16m,n,18] The phosphite complex **12B** gave the highest yields of the substituted products. The acetylferrocenyloxime palladacycles show high activity, though not as active as the acetophenone and benzophenone oxime palladacycles.

Complexes **13A** and **13B** showed high activity for the reaction of aryl bromides with ethyl acrylate and styrene to give 40–88% yield of the substitution products (TON's 2777–91,950). A TON of 91,950 was obtained for the coupling of 1-bromonaphthalene with styrene in the presence of acetophenone oxime carbene complex **13A**. Monomeric phosphine and phosphite analogues **15**, **16** were also prepared for comparison, by the reaction of the dimeric oxime complex **9** with $P(C_6H_5)_3$ (**Cat 15**) and $P(OC_2H_5)_3$ (**Cat 16**).

For the reaction of 1-bromonaphthalene with ethyl acrylate, catalyst **13B** gave the highest yield of 93.2% with a TON of 65,019 and TOF of 9288 $h^{-1}$ compared to the catalyst **15** (yield 65.7%, TON- 49, 773 and TOF- 2074 $h^{-1}$) and catalyst **16** (yield 76.4%, TON- 48, 000 and TOF- 2274 $h^{-1}$). For the reaction with styrene, catalyst **13C** gave the highest yield of 86.8%, TON- of 59, 500 and TOF- of 8500 $h^{-1}$ compared to catalyst **15** (yield 89.3%, TON- 67, 575 and TOF- 2941 $h^{-1}$) and catalyst **16** (yield 82.5%, TON- 51, 725 and TOF- 2343 $h^{-1}$). The carbene complexes gave higher yields, TON's and TOF's compared to the phosphine and phosphite complexes. The results of the Mizoroki–Heck reactions with these catalysts is shown in Table 4. 4-Chlorobenzonitrile and 4-chloroacetophenone reacted with styrene and ethyl acrylate to give 75.7 and 70% yield of the corresponding *E*-stilbenes and *E*-cinnamates (**37**, **38**, 50%)[16q,18] under similar conditions. The TON's obtained for the aryl chlorides were lower (2500–4100) compared to the bromides.

The orthometallated oxime and amine dimeric palladacycle complexes were expected to show better catalytic activity with these NHC's as ligands co-ordinated to the palladacycle. Increased catalytic activity was already observed with the phosphine and phosphite co-ordinated ferrocenyl oxime palladacycles (**Cat 12A**,**B**). Co-ordination of saturated *N*-heterocyclic carbene ligands to the aryl oxime and amine palladacycles increases the thermal, air and moisture stability. The activity of these complexes are similar to previously reported oxime and amine palladacycle complexes and the stability and reactivity is increased by the *N*-heterocyclic carbenes compared to the phosphine ligands.

A comparison of the results with various catalysts and ligands show the high catalyst activity of the palladacycles compared to the bidentate ligands. These catalysts also

**Table 4**. Palladacycles catalyzed reaction of aryl halides

| S. No. | Aryl halide (mmol) | Olefin (mmol) | Catalyst (mmol) | Time (h) | Yield TON | TOF ($h^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | 4-$CH_3O$·$C_6H_4$·I | $C_5H_8O_2$[a] | | | | |
| | (50 mmol) | (100 mmol) | **8** (0.0005) | 8 | 88 (89,540) | 11,190 |
| | (25 mmol) | (50 mmol) | **11** (0.00026) | 12 | 65 (62,500) | 5208 |
| | (25 mmol) | (50 mmol) | **12A** (0.00155) | 12 | 84 (14,000) | 1166 |
| | (25 mmol) | (50 mmol) | **12B** (0.00026) | 12 | 92 (88,461) | 7371 |
| 2 | 4-$CH_3O$·$C_6H_4$·I | $C_8H_8$[b] | | | | |
| | (50 mmol) | (60 mmol) | **8** (0.0005) | 48 | 76 (76,000) | 1740 |
| | | | **9** (0.0005) | 48 | 92 (138,666) | 2888 |
| 3 | $C_6H_5$·I | $C_5H_8O_2$ | | | | |
| | (50 mmol) | (100 mmol) | **9** (0.0005) | 7 | 96 (145,454) | 20,778 |
| 4 | $C_6H_5$·Br | $C_5H_8O_2$ | | | | |
| | (50 mmol) | (100 mmol) | **8** (0.0005) | 34 | 90 (90,000) | 2647 |
| | (50 mmol) | (100 mmol) | **9** (0.0005) | 48 | 52 (72,000) | 240 |
| | (25 mmol) | (55 mmol) | **11** (0.0013) | 24 | 79.3 (15,296) | 276 |
| | (25 mmol) | (55 mmol) | **12A** (0.0015) | 16 | 78 (12,954) | 808 |
| | (25 mmol) | (55 mmol) | **12B** (0.0013) | 24 | 76.6 (10,945) | 456 |
| | (25 mmol) | (30 mmol) | **13A** (0.0004) | 24 | 70 (43,750) | 1823 |
| | (25 mmol) | (50 mmol) | **13B** (0.00036) | 24 | 54.7 (38,055) | 1590 |
| | (25 mmol) | (50 mmol) | **13C** (0.0004) | 24 | 43.5 (27,514) | 1146 |
| 5 | $C_6H_5$·Br | $C_8H_8$ | | | | |
| | (50 mmol) | (60 mmol) | **8** (0.0005) | 29 | 86.6 (86,666) | 2988 |
| | (50 mmol) | (60 mmol) | **9** (0.0005) | 48 | 52 (78,000) | 240 |
| | (50 mmol) | (60 mmol) | **10** (0.0005) | 1 | 96 (483) | 483 |
| | (25 mmol) | (55 mmol) | **11** (0.0013) | 16 | 84 (7000) | 808 |
| | (10 mmol) | (10 mmol) | **12A** (0.0015) | 24 | 79.4 (5480) | 228 |
| | (10 mmol) | (10 mmol) | **12B** (0.0012) | 24 | 83 (7083) | 295 |
| | (25 mmol) | (40 mmol) | **13A** (0.0004) | 24 | 71.6 (41500) | 1729 |
| | (50 mmol) | (60 mmol) | **13B** (0.0004) | 24 | 71.2 (44,500) | 1854 |
| | (25 mmol) | (40 mmol) | **13C** (0.0004) | 24 | 80.1 (50,000) | 2083 |
| 6 | 1-$C_{10}H_7$·Br | $C_5H_8O_2$ | | | | |
| | (10 mmol) | (20 mmol) | **11** (0.0004) | 24 | 83 (31,923) | 1330 |
| | (10 mmol) | (20 mmol) | **12A** (0.0003) | 27 | 86.3 (28733) | 9577 |
| | (10 mmol) | (23 mmol) | **12B** (0.00026) | 8 | 83 (31,994) | 4159 |
| | (25 mmol) | (50 mmol) | **13A** (0.0004) | 21 | 88.4 (55,420) | 2638 |
| | (25 mmol) | (50 mmol) | **13B** (0.00036) | 7 | 93.2 (65,019) | 9288 |
| | (25 mmol) | (50 mmol) | **13C** (0.0004) | 9 | 86.3 (53,925) | 5991 |
| | (25 mmol) | (50 mmol) | **15** (0.00033) | 24 | 65.7 (49,773) | 2074 |
| | (25 mmol) | (50 mmol) | **16** (0.0004) | 21 | 76.4 (48,000) | 2286 |
| 7 | 1-$C_{10}H_7$·Br | $C_8H_8$ | | | | |
| | (10 mmol) | (10 mmol) | **11** (0.00026) | 2 | 94 (36,538) | 11,529 |
| | | (20 mmol) | **12A** (0.0003) | 12 | 91 (30,333) | 2608 |
| | | (10 mmol) | **12B** (0.00036) | 3 | 97 (27,197) | 9065 |
| | (25 mmol) | (30 mmol) | **13A** (0.0002) | 36 | 73.2 (91,950) | 2554 |
| | (25 mmol) | (30 mmol) | **13A** (0.0004) | 36 | 92.6 (61,950) | 1720 |
| | (25 mmol) | (40 mmol) | **13B** (0.00036) | 36 | 77.9 (54,166) | 1504 |
| | (27 mmol) | (35 mmol) | **13C** (0.0004) | 7 | 86.8 (59,500) | 8500 |
| | (25 mmol) | (32 mmol) | **15** (0.00033) | 23 | 89.3 (67,575) | 2938 |
| | (25 mmol) | (32 mmol) | **16** (0.0004) | 22 | 82.5 (51,725) | 2351 |
| 8 | 4-$CH_3O$·$C_6H_4$·Br | $C_8H_8$ | **13A** (0.0016) | 10 | 86.5 (5461) | 546 |
| | (10 mmol) | (20 mmol) | **13B** (0.0014) | 7 | 67.8 (4923) | 703 |
| | | | **13C** (0.0018) | 24 | 50 (2777) | 116 |
| 9 | 4-$NO_2$·$C_6H_4$·Cl | $C_8H_8$ | **8** (0.0005) | 31 | 51 (287) | 9 |
| | (5 mmol) | (10 mmol) | **9** (0.0005) | 30 | 60 (300) | 10 |
| 10 | 4-$NO_2$·$C_6H_4$·Cl | $C_8H_8$ | **8** (0.0005) | 42 | 71 (70,000) | 9 |
| | (50 mmol) | (60 mmol) | **9** (0.0005) | 40 | 69 (350) | 8 |
| 11 | 4-$COCH_3$·$C_6H_4$·Cl | $C_8H_8$ | | | | |
| | (10 mmol) | (16 mmol) | **11** (0.015) | 24 | 30 (38) | 1 |
| | | | **12B** (0.013) | 24 | 53 (81) | 3 |
| | | | **13A** (0.0018) | 24 | 54.9 (3103) | 129 |
| | | | **13B** (0.0023) | 24 | 75.7 (3347) | 139 |
| | | | **13C** (0.001) | 24 | 61.4 (3070) | 128 |
| 12 | 4-CN·$C_6H_4$·Cl | $C_8H_8$ | | | | |
| | (5 mmol) | (6 mmol) | **8** (0.0005) | 20 | 78.5 (350) | 14 |
| | | | **11** (0.009) | 20 | 22 (28) | 1 |
| | | | **12B** (0.0016) | 24 | 37 (58) | 6 |
| | (10 mmol) | (16 mmol) | **13A** (0.0018) | 24 | 73.4 (4111) | 171 |
| | | | **13B** (0.0017) | 24 | 70 (3902) | 162 |
| | | | **13C** (0.002) | 24 | 34 (1705) | 71 |
| 13 | 2-Br·$C_5H_4$·N | $C_5H_8O_2$ | | | | |
| | (5 mmol) | (10 mmol) | **9** (0.0005) | 48 | 68 (4090) | 85 |

[a] Styrene.
[b] Ethyl acrylate.

show high TON and TOF. Use of co-catalysts $(C_4H_9)_4NBr$, $(C_4H_9)_4NI$, Lewis acids $ZnCl_2$ and $AlCl_3$ activate aryl chlorides to give moderate yields. The absence of back bonding (available in the P-ligands) and the σ-donor ability of the N-ligands, causes activation of aryl and vinyl halides in the oxidation addition reactions by assisting in the labilization of the bromides and chlorides. The electron rich ferrocenyl oxime ligands, *N*-palladacycles, NHC's, phosphites, DAB, could be activating ligands, which increase the electron density at the metal. This effect was most successful with the palladacycles and the DAB Pd complexes while the ferrocenyl palladacycle though active did not show the expected high TON and TOF.

## 3. Experimental

### 3.1. General

The aryl halides, styrene, ethyl acrylate, glyoxal, ligands and the metal complexes were purchased or prepared according to known procedures.[12] The reactions were monitored by TLC using GF-254 grade silica gel on glass plates. Silica gel (100–200 mesh) was used for column chromatography. The products, intermediates and metal complexes were characterized by spectroscopic methods (IR, NMR, MS) and C, H analysis. $^1H$, $^{13}C$ NMR spectra were recorded in $CDCl_3$ on 200 and 300 MHz NMR instruments. All reactions were carried out under Ar atmosphere.

**3.1.1. Preparation of acetophenone oxime, (2-*C*,*N*) chloro(1,3-diphenylimidazolidin-2-ylidene)palladacycle (II).**[13,18] 0.2 g (0.4 mmol) of acetophenone oxime palladacycle and 0.16 g of dimeric carbene were refluxed in 5 ml dry *m*-xylene at 120–130 °C for 2 h. A yellow precipitate was formed, filtered and dried. The separated solid was recrystallized from dichloromethane and hexane mixture to get a yellow crystalline powder. Yield: 0.131 g (33%), $^1H$ NMR (δ, $CDCl_3$, 200 MHz) 9.96 (s, 1H, O*H*), 8.04–8.00 (m, 4H, *Ar*), 7.5–6.6 (m, 15H, *Ar*), 4.5–4.2 (m, 4 H, C$H_2$), 2.26 (s, 3H, C$H_3$); IR ($cm^{-1}$, Nujol): 3163 ($\nu_{O-H}$), 1284 ($\nu_{C-N}$); CHN—analysis calculated (found) for $C_{23}H_{22}N_3OClPd$: C, 55.4 (55.3), H, 4.5 (4.53), N, 8.4 (8.38).

**3.1.2. Preparation of chloro(*N*,*N*-dimethylbenzylamine, 2-*C*,*N*) (1,3-diphenylimidazolidin-2-ylidene)palladium (II).**[13,18] 0.08 g (0.147 mmol) of *N*,*N*-dimethylbenzylamine palladacycle and 0.066 g of dimeric carbene were refluxed in 5 ml dry *m*-xylene at 120–130 °C for 2 h. The solution was filtered, concentrated and recrystallized from dichloromethane and petroleum ether mixture to get white microcrystalline complex. Yield: 0.03 g (21%), mp: >200 °C, IR ($cm^{-1}$, Nujol): 1280 ($\nu_{C-N}$); $^1H$ NMR (δ, $CDCl_3$, 200 MHz) 8.14–6.61 (m, 14H, *Ar*), 4.34–4.32 (m, 4H, C$H_2$), 3.61 (s, 2H, C$H_2$), 2.60 (s, 6H, N(C$H_3$)$_2$); CHN—analysis calculated (found) for $C_{24}H_{26}N_3ClPd$: C, 57.8 (57.92), H, 5.26 (5.27), N, 8.43 (8.24).

**3.1.3. Reaction of aryl halide with olefins (Cat-1–10).**[18] 4-Iodoanisole (0.234 g, 1 mmol), ethyl acrylate (0.28 g, 3 mmol), catalyst-**1** {Pd(DMG)$Cl_2$, 0.025 g, 0.09 mmol} and $K_2CO_3$ (0.276 g, 2 mmol) were taken in a flask with NMP as solvent (6 ml) and the reaction mixture heated to 140 °C for 6 h. After completion of the reaction, monitored by TLC for complete consumption of the aryl halide, the reaction mixture was poured into dilute HCl (25 ml, 10% solution) and extracted with ethyl acetate (3×25 ml). The combined organic fraction was washed with saturated brine, dried over anhydrous $Na_2SO_4$ and concentrated on a rotary evaporator. Purification by column chromatography over silica gel (100–200 mesh) gave the 2-propenoic acid, 3-(4-methoxyphenyl)-, ethyl ester (**18**, 0.165 g, 80% yield, mp: 47–48.8 °C).[16a] $^1H$ NMR (200 MHz, $CDCl_3$, δ): 7.68–7.61 (d, 1H, *J*=14 Hz, Ar·C*H*═), 7.50–7.46 (d, 2H, *J*=8 Hz, Ar-$H_3$, $H_5$), 6.92–6.88 (d, 2H, *J*=8 Hz, Ar-$H_2$, $H_6$), 6.35–6.27 (d, 1H, *J*=16 Hz, ═C*H*·COO$C_2H_5$), 4.31–4.20 (q, 2H, *J*=8 Hz, –COO$CH_2$·), 3.84 (s, 3H), 1.37–1.30 (t, 3H, *J*=8 Hz, $COOCH_2$·C$H_3$); IR ($cm^{-1}$, Nujol): 2977, 2939, 2839, 1712, 1635, 1512, 1365, 1303, 1250, 1170, 1033, 979, 833, 555, 524; MS (*m*/*e*): 206, 191, 178, 161, 147, 134, 126, 118, 103, 89, 81, 77.

**3.1.4. Reaction of 4-iodo anisole with ethyl acrylate catalyzed by palladacycle 8.**[18] 4-Iodoanisole (11.7 g, 50 mmol), ethyl acrylate (10 g, 100 mmol), $K_2CO_3$ (8.28 g, 60 mmol) and 50 ml *N*-methylpyrrolidinone were taken in a round bottomed flask and the Pd complex **8** (0.00027 g, 0.0005 mmol) was added as catalyst. The reaction mixture was heated in a oil bath maintained at 150 °C for 8 h. The usual extractive workup with dilute HCl followed by purification over silica gel (100–200 mesh) to give 2-propenoic acid, 3-(4-methoxyphenyl)-, ethyl ester (**18**, 9.223 g, 88.3%, TON- 89, 540, TOF- 11, 192 $h^{-1}$).

**3.1.5. Reaction of 1-bromonaphthalene with styrene catalyzed by Pd(Cy-DAB)$Cl_2$ (Cat-4) (27).**[18] 5.175 g (25 mmol) of 1-bromonaphthalene was taken in a flask and styrene (3.03 g, 30 mmol), 25 ml *N*-methylpyrrolidinone added to it followed by 2.49 g (30 mmol) of $CH_3COONa$ and 0.00022 g (0.0004 mmol) of the (**Cat-4**) catalyst. The reaction mixture was heated to 140–150 °C in an oil bath till the bromo naphthalene was completely consumed (36 h). Dilute HCl was added to the reaction mixture and extracted with ethyl acetate (3×100 ml). Washing with brine, drying over anhydrous $Na_2SO_4$, concentration on a rotary evaporator and purification by column chromatography (silica gel: 100–200 mesh) gave 5.32 g (**27**, 92.6%, TON, 61,956, mp: 69.9–70.9 °C)[16i] of naphthalene, 1-[(1*E*)-2-phenylethenyl]- (**27**). $^1H$ NMR (200 MHz, $CDCl_3$, δ): 8.28–7.14 (m, 14H); IR ($cm^{-1}$, Nujol): 1595, 1377, 1350, 1141, 1074, 1012, 968, 956, 792, 773, 754, 690; MS (*m*/*e*): 230, 215, 202, 189, 176, 152, 141, 128, 115, 107, 101, 91, 77.

**3.1.6. Reaction of bromobenzene with styrene catalyzed by Pd(dba)$_2$/(Cy-DAB) (Cat-4A) (25).**[18] Bromobenzene (7.85 g, 50 mmol) was taken in a flask and styrene (5.2 g, 50 mmol), 15 ml *N*-methylpyrrolidinone added to it followed by 7.59 g (55 mmol) of $K_2CO_3$, 0.00011 g (0.0002 mmol) of the **Cat-4A**, and 0.00008 g (0.0004 mmol) of cyclohexyl DAB. The reaction mixture was heated to 140 °C in an oil bath for 48 h. Dilute HCl was added to the reaction mixture and extracted with ethyl acetate (3×100 ml). Washing with brine, drying over anhydrous $Na_2SO_4$, concentration on a rotary evaporator

and purification by column chromatography (silica gel: 100–200 mesh) gave 1.354 g (**25**, 15%, TON- 37, 600)[16g] of Benzene, 1,1′-(1,2-ethenediyl)bis- (**25**), mp: 120 °C, $^1$H NMR (200 MHz, $CDCl_3$, $\delta$): 7.5–7.1 (m, 12H, *Ar*, C*H*═); IR ($cm^{-1}$, Nujol): 1596, 1377, 1330, 1296, 1220, 1155, 1072, 1027, 963, 962, 908, 765, 692; MS (*m*/*e*): 180, 165, 152, 139, 126, 115, 102, 89, 76.

**3.1.7. Reaction of 1-bromonaphthalene with styrene catalyzed by benzophenone oxime, (2-*C*,*N*) chloro(1,3-diphenylimidazolidin-2-ylidene)palladacycle (II) (Cat-13B) (27).**[18] 5.175 g (25 mmol) of 1-bromonaphthalene was taken in a flask and styrene (3.03 g, 30 mmol), 25 ml *N*-methylpyrrolidinone added to it followed by 2.49 g (30 mmol) of $CH_3COONa$ and 0.00022 g (0.0004 mmol) of the (**Cat-13B**) benzophenone oxime palladacycle carbene catalyst. The reaction mixture was heated to 140–150 °C in an oil bath till the bromo naphthalene was completely consumed (36 h). Dilute HCl was added to the reaction mixture and extracted with ethyl acetate (3×100 ml). Washing with brine, drying over anhydrous $Na_2SO_4$, concentration on a rotary evaporator and purification by column chromatography (silica gel: 100–200 mesh) gave 5.32 g (92.6%, TON- 61, 956) of Naphthalene, 1-[(1*E*)-2-phenylethenyl]- (**27**).

**3.1.8. Di-μ-chlorobis(benzophenoneoxime)dipalladium/$AlCl_3$ catalyzed vinylation of 4-chlorotoluene with styrene (35).**[18] Styrene (0.416 g, 4 mmol) and 4-chlorotoluene (0.252 g, 2 mmol)) were taken in a flask and the catalyst **10** (0.01 g, 0.01 mmol), tributyl amine (0.741 g, 4 mmol) and tetrachloroethane (10 ml) as solvent was added. The solution was cooled in an ice bath and $AlCl_3$ (0.266 g, 2 mmol) was added to the reaction mixture. Refluxing for 72 h and the usual work up gave the benzene, 1-methyl-4-[(1*E*)-2-phenylethenyl]- (**35**, 0.150 g, 39%, mp: 120 °C).[17p]

**3.1.9. Di-μ-chlorobis(benzophenoneoxime)dipalladium/$(C_4H_9)_4NI$ catalyzed vinylation of 4-chlorotoluene with styrene (35).**[18] Styrene (0.416 g, 4 mmol), 4-chlorotoluene (0.254 g, 2 mmol), $(C_4H_9)_4NI$ (0.738 g, 2 mmol), $K_2CO_3$ (0.552 g, 4 mmol) were taken in a flask and the catalyst **10** (0.015 g, 0.01 mmol) added to it. 1-Methylpyrrolidinone (5 ml) was added as solvent and the reaction mixture heated to 130 °C for 24 h. Usual work up gave the benzene, 1-methyl-4-[(1*E*)-2-phenylethenyl]- (**35**) (0.095 g, 28%).

**3.1.10. Reaction of 4-chlorobenzonitrile with styrene catalyzed by carbene palladacycle (13A) (33).**[18] 4-Chlorobenzonitrile (1.393 g, 10.17 mmol), styrene (1.709 g, 16.4 mmol) were taken in a flask and 10 ml of *N*-methylpyrrolidinone added to it. NaOAc (1.098 g, 12.5 mmol), $(C_4H_9)_4NBr$ (0.322 g, 1 mmol) and acetophenone oxime palladacycle carbene (**13 A**, 0.0009 g, 0.0018 mmol) was added to it as catalyst and the reaction mixture heated to 140 °C for 24 h until all the starting material was completely consumed. Added water, extracted with ethyl acetate, the combined organic extracts washed with brine, dried over anhydrous $Na_2SO_4$ and concentrated on a rotary evaporator. Purification by column chromatography gave 1.526 g (**33**, 73.4%, TON- 4111)[16m] of benzonitrile, 4-[(1*E*)-2-phenylethenyl]- (**33**), mp: 117.4–117.7 °C, $^1$H NMR (200 MHz, $CDCl_3$, $\delta$): 7.8–6.8 (m, 11H, *Ar*, C*H*═); IR ($cm^{-1}$, Nujol): 2852, 2225, 1602, 1504, 1377, 1166, 966, 873, 823, 757, 690; MS (*m*/*e*): 205, 190, 176, 165, 151, 139, 127, 113, 102, 89, 76, 63.

**3.1.11. Reaction of 4-chloroacetophenone with styrene catalyzed by carbene palladacycle (13B) (32).**[18] 4-Chloroacetophenone (1.57 g, 10.2 mmol), styrene (1.680 g, 16.1 mmol) were taken in a flask and 10 ml of *N*-methylpyrrolidinone added to it. NaOAc (1.06 g, 13 mmol), $(C_4H_9)_4NBr$ (0.322 g, 1 mmol) and benzophenone oxime palladacycle carbene (**13B**, 0.0023 g, 0.0023 mmol) was added to it as catalyst and the reaction mixture heated to 140 °C for 24 h until all the starting material was completely consumed. Added water, extracted with ethyl acetate, the combined organic extracts washed with brine, dried over anhydrous $Na_2SO_4$ and concentrated on a rotary evaporator. Purification by column chromatography gave 1.71 g (75.7%, TON- 3347, mp: 148–150 °C)[16n] of ethanone, 1-[4-(2-phenylethenyl)phenyl]- (**32**). $^1$H NMR (200 MHz, $CDCl_3$, $\delta$): 7.97–7.93 (d, 2H, *J*=8 Hz, Ar-$H_{2,6}$), 7.61–7.25 (m, 7H, *Ar*·C*H*═), 7.20–7.16 (d, 2H, *J*=8 Hz, Ar-$H_{3,5}$), 2.61 (s, 3H); IR ($cm^{-1}$, Nujol): 2854, 1677, 1600, 1409, 1357, 1265, 1178, 1074, 966, 867, 821, 756, 725, 692, 592; MS (*m*/*e*): 222, 207, 178, 165, 152, 139, 126, 115, 102, 96, 89, 76, 63, 57.

**3.1.12. Reaction of 4-bromo-*N*,*N*-dimethyl aniline with styrene in *N*-methyl pyrrolidinone (13B).**[18] 4-Bromo-*N*,*N*-dimethyl aniline (0.395 g, 2 mmol), styrene (0.249 g, 2.4 mmol), $K_2CO_3$ (0.552 g, 4 mmol) were taken in a flask and 6 ml of *N*-methylpyrrolidinone added to it followed by (0.01 g, 0.017 mmol) of the catalyst (**Cat-6**) and the reaction mixture heated to 140–150 °C for 24 h until all the starting material was completely consumed. Added water, extracted with ethyl acetate, the combined organic extracts washed with brine, dried over anhydrous $Na_2SO_4$ and concentrated on a rotary evaporator. Purification by column chromatography (Silica gel: 100–200 mesh) gave 0.28 g (**30**, 63%, TON- 73, mp: 147.6–148.7 °C)[16l] of benzenamine, *N*,*N*-dimethyl-4-(2-phenylethenyl)-, (*E*) (**30**) $^1$H NMR (200 MHz, $CDCl_3$, $\delta$): 7.5–7.15 (m, 9H, *Ar*), 7.02–6.94 (d, *J*=16 Hz, 1H, *Ar*·C*H*═), 6.74–6.69 (d, *J*=10 Hz, 1H, $C_6H_5$–C*H*), 2.98 (s, 6H, $N(CH_3)_2$); IR ($cm^{-1}$, Nujol): 2923, 2852, 1604, 1519, 1461, 1352, 1222, 966, 810, 748, 690; MS (*m*/*e*): 223, 207, 193, 178, 165, 152, 128, 111, 89, 77.

**3.1.13. Reaction of bromobenzene with butyl acrylate in ionic liquid-$(C_4H_9)_4NBr$ (34).**[18] $(C_4H_9)_4NBr$ (1.932 g, 6 mmol) was taken in a flask and bromobenzene (0.571 g, 3 mmol), butyl acrylate (0.384 g, 3 mmol), $HCOONH_4$ (0.012 g, 0.2 mmol), $Na_2CO_3$ (0.636 g, 6 mmol) and **Catalyst-4** (0.012 g, 0.03 mmol) added to it. The reaction mixture was heated to 130 °C for 24 h. Usual extractive workup followed by purification by column chromatography gave 0.430 g, 70% yield of the (*E*)-2-propenoic acid, 3-phenyl-, butyl ester (**34**) (TON- 70).[16o] $^1$H NMR (200 MHz, $CDCl_3$, $\delta$): 7.73–7.65 (d, 1H, *J*=16 Hz, Ar·C*H*═), 7.56–7.31 (m, 5H), 6.49–6.41 (d, 1H, *J*=16 Hz, ═C*H*·$COOC_4H_9$), 4.25–4.18 (t, 2H, *J*=6 Hz, –$COOCH_2$·$C_3H_7$), 2.05 (s, 3H), 1.80–1.35 (m, 4H, –$COOCH_2$·$CH_2$·$CH_2$·$CH_3$), 1.01–0.93 (t, 3H, *J*=8 Hz,

$-COOCH_2CH_2CH_2{\cdot}CH_3$); IR ($cm^{-1}$, Nujol): 3060, 3028, 2958, 2933, 2873, 1712, 1639, 1311, 1280, 1170, 1066, 979, 864, 767, 709, 684.

**3.1.14. Reaction of 4-bromo-*N*,*N*-dimethyl aniline with ethyl acrylate in ionic liquid-$(C_4H_9)_4NBr$ (29).**[18] $(C_4H_9)_4NBr$ (2 g, 6.2 mmol) was taken in a flask and 4-bromo-*N*,*N*-dimethyl aniline (0.395 g, 2 mmol), ethyl acrylate (0.4 g, 4 mmol), HCOONa (0.010 g, 0.147 mmol), $NaOCOCH_3$ (0.196 g, 2.4 mmol) and **Catalyst-6** (0.010 g, 0.022 mmol) added to it. The reaction mixture was heated to 130 °C for 15 h. Usual extractive workup followed by purification by column chromatography gave 0.25 g, 57.3% yield (**29**, TON- 50, mp: 76.3–77.8 °C)[16k] of the 2-propenoic acid, 3-[4-(dimethylamino)phenyl]-, ethyl ester (**29**) $^1H$ NMR (200 MHz, $CDCl_3$, $\delta$): IR ($cm^{-1}$, Nujol): 7.68–7.60 (d, 1H, $J$=16 Hz, Ar·C*H*=), 7.46–7.41 (d, $J$=8 Hz, 2H, *Ar*), 6.70–6.66 (d, $J$=8 Hz, 2H, *Ar*), 6.28–6.20 (d, $J$=16 Hz, 1H, Ar·C*H*=), 4.27–4.20 (q, 2H, $J$=6 Hz, $-COOCH_2{\cdot}CH_3$), 3.03 (s, 6H, $N(CH_3)_2$), 1.37–1.31 (t, $J$=6 Hz, 3H, $-COOCH_2{\cdot}CH_3$); IR ($cm^{-1}$, Nujol): 2923, 2854, 1704, 1600, 1525, 1456, 1367, 1305, 1220, 985, 813; MS (*m*/*e*): 219, 190, 174, 146, 130, 118, 102, 98, 87, 72.

## Acknowledgements

We thank the DST for research funds, CR, GMK the CSIR for SRF's, D.K.K., A.J., V.V.T. and S.S. for some preliminary experiments.

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18. Registry numbers of the products: 1. 2-Propenoic acid, 3-(4-methoxyphenyl)-, ethyl ester (**18**) (1929-30-2) 2. 2-Propenoic acid, 3-(4-chlorophenyl)-, ethyl ester, (*E*) (**19**) (24393-52-0) 3. 2-Propenoic acid, 3-phenyl-, ethyl ester, (2*E*) (**20**) (4192-77-2) 4. Phenol, 4-(2-phenylethenyl (**21**) (3839-46-1) 5. Benzene, 1-methoxy-4-[(1*E*)-2-phenylethenyl]- (**22**) (1694-19-5) 6. 2-Propenoic acid, 3-(4-nitrophenyl)-, ethyl ester (**23**) (953-26-4) 7. 2-Propenoic acid, 3-(2-pyridinyl)-, ethyl ester, (2*E*)- (**24**) (70526-11-3) 8. Benzene, 1,1(-(1,2-ethenediyl)bis- (**25**) (103-30-0) 9. 2-Propenoic acid, 3-(1-naphthalenyl)-, ethyl ester, (*E*)- (**26**) (98978-43-9) 10. Naphthalene, 1-[(1*E*)-2-phenylethenyl]- (**27**) (2840-87-1) 11. 2-Propenoic acid, 3-(4-hydroxyphenyl)-, ethyl ester (**28**) (2979-06-8) 12. 2-Propenoic acid, 3-[4-(dimethylamino)phenyl]-, ethyl ester (**29**) (1552-97-2) 13. Benzenamine, *N*,*N*-dimethyl-4-(2-phenylethenyl)-, (*E*) (**30**) (838-95-9) 14. Benzene, 1-nitro-4-[(1*E*)-2-phenylethenyl (**31**) (1694-20-8) 15. Ethanone, 1-[4-(2-phenylethenyl)phenyl]- (**32**) (3112-03-6) 16. Benzonitrile, 4-[(1*E*)-2-phenylethenyl]- (**33**) (13041-79-7) 17. 2-Propenoic acid, 3-phenyl-, butyl ester (**34**) (538-65-8) 18. Benzene, 1-methyl-4-[(1*E*)-2-phenylethenyl]- (**35**) (1860-17-9) 19. Benzene, 1-chloro-4-[(1*E*)-2-phenylethenyl] (**36**) (1657-50-7) 20. 2-Propenoic acid, 3-(4-cyanophenyl)-, ethyl ester, (*E*)- (**37**) (62174-99-6) 21. 2-Propenoic acid, 3-(4-acetylphenyl)-, ethyl ester,(*E*) (**38**) (82989-26-2); 22. **Cat-13B**–palladium,chloro(1,3-diphenyl-2-imidazolidinylidene)[2-[(hydroxyimino)phenylmethyl]-phenyl-*C*,*N*]-, (SP-4-4)-$C_{28}H_{24}ClN_3OPd$-(68248-78-2); 23. **Cat-10**–palladium, di-μ-chlorobis[2-[1-(hydroxyimino)-ethyl]phenyl-*C*,*N*]di-, stereoisomer–$C_{16}H_{16}Cl_2N_2O_2Pd$-(32679-19-9); 24. **Cat-8**–palladium, di-μ-chlorobis[2-[(dimethylamino-*N*)methyl]phenyl-*C*]di- $C_{18}H_{24}Cl_2N_2Pd_2$-(18987-59-2); 25. **Cat-13A**–palladium, chloro(1,3-diphenyl-2-imidazolidinylidene)[2-[1-(hydroxyimino)ethyl]phenyl-*C*,*N*]-, (SP-4-4)-$C_{23}H_{22}ClN_3OPd$-(68248-77-1); 26. **Cat-13B**–palladium,chloro(1,3-diphenyl-2-imidazolidinyl-idene)[2-[(hydroxyimino)phenylmethyl]phenyl-*C*,*N*]-, (SP-4-4)-$C_{28}H_{24}ClN_3OPd$-(68248-78-2); 27. **Cat-13C**–palladium, chloro[2-[(dimethylamino)methyl]phenyl-*C*,*N*](1,3-diphenyl-2-imidazolidinylidene)-, (SP-4-4)- $C_{24}H_{26}ClN_3Pd$ -(68248-79-3).