

Bimetallic Ni–Pd Synergism—Mixed Metal Catalysis of the Mizoroki-Heck Reaction and the Suzuki–Miyaura Coupling of Aryl Bromides

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Received: 26 May 2020 / Accepted: 21 July 2020 © Springer Science+Business Media, LLC, part of Springer Nature 2020

Abstract

A combination of Pd and Ni complexes activated aryl bromides for the thermal Mizoroki-Heck reaction and Suzuki coupling giving high yields in short reaction times. A thermal redox mechanism probably occurs whereby Ni complex transfers electron and reduces the Pd (II) to Pd (0) which then takes the reactants through the standard protocol of oxidative-addition, migratory insertion and reductive elimination, typical for the Mizoroki-Heck reaction and the Suzuki coupling.

Graphic Abstract



 $R: H, 4\text{-}CH_{3}O, 4\text{-}CH_{3}, 4\text{-}Cl, 4\text{-}OH, 1\text{-}Nap, 4\text{-}C_{6}H_{5} \quad W: COOC_{2}H_{5}, C_{6}H_{5}$

 $\textbf{Keywords} \ \ Bimetallic \ catalysis \cdot Mizoroki-Heck \cdot Suzuki \ coupling \cdot Nickel \ complexes \cdot Pd(OAc)2$

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10562-020-03330-9) contains supplementary material, which is available to authorized users.

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1 Introduction

Synergistic interaction of bimetallic catalysts cause increased activity & efficiency compared to monometallic catalysis [1]. State of the art, bimetallic nano alloy architectures demonstrate conservatism in the noble metal usage and increased catalyst activity. Bimetallic nano clusters conjure a magical wizardry associated with catalyst activation known for the efficient catalysis of several reactions [2–20]. No studies with mixed metal complexes is reported for the Mizoroki-Heck reaction or Suzuki coupling. The activation of aryl bromides and chlorides is essential atom economy in several cross coupling reactions thus making them suitable for industrial applications [21]. The use of tert-Bu₃P,

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phosphite ligands, additives like PPh_4Cl , dimethyl glycine, NHC ligands, special sterically bulky ligands and bases, palladacycles, ionic liquids are some of the solutions for aryl bromide and chloride activation for the Mizoroki-Heck reaction and Suzuki–Miyaura coupling [22–46].

Bimetallic nano alloys of noble metal Pd merged with non noble metal Fe, Co, Ni ramps up catalysis for various reactions like hydrogenation. Here, noble metal usage is conserved leading to an inexpensive alternative and merger with non noble metal conjuring a magical boosting of activity and efficiency [12–25]. Bozell and Vogt exploited this synergism of NiBr₂ with Pd(OAc)₂ as bimetallic catalyst for the Mizoroki-Heck reaction of aryl chlorides but requiring addition of excess NaI [47]. Ni complexes, Cu salts and heterogeneous Ni, Cu, Co and Mn are good catalysts for the Mizoroki-Heck reaction of aryl iodides and bromides [48-53]. Ligand free Pd(OAc)₂ has been reported to catalyze the Mizoroki-Heck reaction of aryl bromides requiring long reaction times of 19–44 h [54]. In related studies in our laboratory, bimetallic catalyst systems of Ni-Pd-supported on ABPBI (polybenzimidazole) polymer and Ni-Pd QD (quantum dots) were used to catalyze the Mizoroki-Heck reaction and Suzuki-Miyaura coupling of aryl halides [55, 56]. Bimetallic Ni-Pd alloys have demonstrated enhanced activity in Sonogashira coupling and Suzuki coupling [12, 15, 57, 58]. This enhanced activity can be explained as being due to a redox couple with electron transfer from Ni to Pd which generates high electron density on Pd and thus enhances reduction of Pd (II) to Pd (0). This increases the rate of oxidative addition step in the catalytic cycle [15]. Based on this we proposed the conservative synergism of Ni complexes with $Pd(OAc)_2$ for the activation of aryl bromides for the Mizoroki-Heck reaction and the Suzuki-Miyaura coupling. Ligands on Nickel and Pd would thus enhance the reactivity enabling the electron transfer from Ni to Pd.

Recently, the use of Ni–Pd binary nanoclusters for the Suzuki–Miyaura coupling of hindered, ortho-heterocycle tethered, aryl bromides and carbonates has been reported [59, 60]. In this letter we describe the bimetallic catalysis of the thermal Mizoroki-Heck reaction and Suzuki coupling with a mixture of Ni and Pd metal salts and complexes, showing enhanced activity.

2 Experimental Procedures

2.1 General Procedure for Bimetallic Catalysis of Mizoroki-Heck Reaction of Various Aryl Bromides

To a solution of aryl bromide (1 mmol), alkene (1-2 mmol), TBABr (Tetrabutylammonium bromide) (1 mmol) and base (1.2 mmol) in NMP (1-methyl-2-pyrrolidinone) (5 ml) was added [Pd] (2.5 mol %) and Ni complex (5 mol %). After degassing with argon, the resulting mixture was heated with stirring at 150 °C for 1–12 h under argon. After completion of reaction (monitored by TLC), the reaction mixture was quenched by adding 10% HCl. The solution was extracted with ethyl acetate (3×20 ml) the combined extract was washed with saturated brine and dried over anhydrous Na₂SO₄. The organic layer was concentrated under vacuum and the crude product purified by column chromatography on silica gel (100–200 mesh, Petroleum ether or Petroleum Ether: 2–5% Ethyl acetate) to give pure product.

Benzene, 1-methoxy-4- [(1E)-2-phenylethenyl]- (6 h, 0.151 g, 72%, 0.72 mmol, White solid, MP-136 °C) CAS Registry Number 1694–19-5 2 ¹H NMR (CHLOROFORM-d, 200 MHz): δ (ppm) 7.31–7.69 (m, 7H), 7.17 (d, *J*=7.5 Hz, 2H), 7.05 (d, *J*=8.7 Hz, 2H), 3.97 (s, 3H); ¹³C NMR (CHLO-ROFORM-d, 50 MHz): δ (ppm) 159.4, 137.7, 130.2, 129.5, 128.7, 128.4, 128.4, 128.3, 128.2, 127.8, 127.7, 127.3, 126.7, 126.3, 114.2, 113.6, 113.0, 77.7, 77.1, 76.5, 55.4; IR (cm⁻¹) 2920, 2854, 2344, 2288, 1605, 1384, 1313, 1120, 1038, 865, 773, 714, 661; HRMS-ESI: [M⁺ + H]⁺ calcd for C₁₅H₁₅O, 211.112 found: 211.111.

2.2 General Procedure for the Bimetallic (Ni–Pd) Catalysis of Aryl Bromides for the Suzuki Coupling

To a solution of aryl halide (0.5 mmol), aryl boronic acid (0.073 g, 0.6 mmol), TBABr (0.161 g, 0.5 mmol) and K_3PO_4 (0.127 g, 0.6 mmol) in dioxane and water (1:1, 10 ml) was added Pd(OAc)₂ (0.005 g, 0.03 mmol, 2.5 mol%) and [Ni] complex (5 mol%). The resulting mixture was heated with stirring at 130 °C for 2–6 h under argon. After completion of reaction (monitored by TLC), the reaction mixture was quenched with 10% HCl. The solution was extracted with ethyl acetate (3×20 ml) the combined extract was washed with saturated brine and dried over anhydrous Na₂SO₄. The organic layer was concentrated under vacuum and the crude product purified by column chromatography on silica gel (100–200 mesh, Petroleum Ether) to give pure product.

1,1'- Biphenyl, 4-methyl- (4.5 h, 0.076 g, 0.45 mmol, 90% yield, white solid, MP–49 °C) CAS Registry Number 644-08-6 ¹H NMR (CHLOROFORM-d, 200 MHz): δ =7.17–7.63 (m, 9 H), 2.39 ppm (s, 3 H); IR (cm⁻¹)–2926, 2372, 2112, 1592, 1413, 1122, 1043, 859, 814, 752; HRMS-ESI: [M⁺+H]⁺ calcd for C₁₃H₁₃ [M⁺+H]⁺ 169.102 found: 169.101.

3 Results and Discussion

Preliminary screening with various Ni complexes and $Pd(OAc)_2$ showed the bimetallic complexes to be active for the Mizoroki-Heck reaction of 4-bromo anisole and ethyl

Scheme 1 Ni–Pd catalyzed Mizoroki-Heck reaction of 4-bromoanisole with ethyl acrylate



H₅ K_2CO_3 , TBABr NMP, 150 °C Yield : 37 - 92 %, E

COOC₂H₅

Pd(OAc)2 2.5.mol %

 Table 1
 Ni–Pd catalyzed Mizoroki-Heck reaction of 4-bromoanisole with ethyl acrylate

S. No.	Cat-A	Cat-B	Time (h)	Yield (%) (E)
1	Pd(OAc) ₂	None	48	63
2	Pd(OAc) ₂ -PPh ₃	None	18	53
3	Pd(OAc) ₂	Ni[P(OPh)3]4	1	62
4	HB-PdCycle	$Nibpy_3Cl_2$	1.3	77
5	Pd(OAc) ₂	Nien ₃ Cl ₂	1.3	51
6	Pd(OAc) ₂	Ni[DMG] ₂	1.5	37
7	PdCl ₂ (CH ₃ CN) ₂	Ni-[8-HQ] ₂	2.30	67
8	PdCl ₂ (PPh ₃) ₂	Ni[P(OPh3)]4	3.3	78
9	Oxime PdCycle	NiCl ₂ (PPh ₃) ₂	3.30	58
10	Pd(OAc) ₂	NiCl ₂ (PPh ₃) ₂	6	78
11	Bedford-PdCycle	Nien ₃ Cl ₂	10.1	76
12	$Pd(OAc)_2$	[Ni(acac) ₂] ₃	13.5	92
13	Pd(OAc) ₂	NiBr ₂	14.5	63
14	$Pd[P(OPh)_3]_4$	$Nibpy_3Cl_2$	22	45
15	Pd(OAc) ₂	NiSalen	24	52
16	Pd(OAc) ₂	Ni-[8-HQ] ₂	25	80
17	Pd(OAc) ₂	$Nibpy_3Cl_2$	26	78
18	Pd(OAc) ₂	NiSalphen	36	54

Reaction conditions: 4-Bromoanisole (1 mmol), Ethylacrylate (1–2 mmol), K_2CO_3 (1.2 mmol), TBABr (1 mmol), Pd Cat (2.5 mol %), Ni (Co-Cat) (5 mol %), NMP (5 ml), Argon

acrylate (Scheme 1). Moderate to high yields were obtained (Table 1) and the results are shown in increasing time of reaction. A standard protocol for the Mizoroki-Heck reactions was used for these bimetallic catalyzed reactions in NMP as solvent. The reaction catalyzed by Ni[P(OPh)₃]₄ & $Pd(OAc)_2$ was the fastest being complete in 1 h with high yield of 62% E-isomer. Ni(bpy)₃Cl₂ was completed in 1.3 h but moderate yield of 51%. But the use of Herrmann-Beller Pdcycle with Nibpy₃Cl₂ gave higher yield of 77% in 1.3 h. Reaction times of 1.5-6 h was achieved with Ni[DMG]₂ (Ni-Dimethylglyoxime), Ni[8-HQ] (Ni-8-Hydroxyquinoline), Ni[P(OPh)₃]₄, and NiCl₂(PPh₃)₂ with yields in the range of 51–78%. The Pd catalysts were Pd(OAc)₂, PdCl₂(CH₃CN)₂, PdCl₂(PPh₃)₂, and Oxime PdCycle. The reaction with Oxime Pdcycle gave a lower yield of 58% compared to the catalysis with $Pd(OAc)_2$ which gave 78% yield but in 6 h, longer time. The reaction with $[Ni(acac)_2]_3$ gave the highest yield of 92% in 13.5 h. NiBr₂, Nibpy₃Cl₂ (bpy-bipyridyl) Ni Salen, Ni- $[8-HQ]_2$ Ni Salphen, in conjunction with Pd(OAc)₂ took longer times of 14.5–36 h with good yields of 45–80%.



R : H, 4-CH₃O, 4-CH₃, 4-Cl, 4-OH, 1-Nap, 4-C₆H₅ W : COOC₂H₅, C₆H₅

Scheme 2 Ni–Pd catalyzed Mizoroki-Heck reaction of various aryl bromides

From these results one could assume that $P(OPh)_3$, PPh_3 are very good ligands on Ni in conjunction with $Pd(OAc)_2$ while bpy is equally good but taking longer reaction times of 26 h. NiSalen and Ni SALPHEN both gave lower yields of 52–54% requiring longer reaction times also of 24–36 h. This phenomena could be due to higher electron density attributed to the phosphine ligands compared to the nitrogen ligand; while use of palladacycles gives better yields in shorter times. All these results were from unoptimized reactions. The reaction catalyzed by $Pd(OAc)_2$ only, with no Ni co-catalyst, proceeded slowly in 48 h and moderate yield of 63% [54]. Addition of PPh_3 as ligand reduced the reaction time to 18 h with yield of 53%.

The reaction of different aryl bromide with styrene and ethyl acrylate was then experimented with combinations of Pd and Ni complexes (Scheme 2; Table 2). A 1:2 ratio of Pd to Ni complexes was effective catalyst. A 1: 10 ratio was also found effective for the Mizoroki-Heck reaction of 4-bromo anisole and ethyl acrylate. Apart from Pd(OAc)₂, we also tried some Pd complexes and palladacycles as catalysts along with different Ni complexes as co-catalyst. The Herrmann Pd cycle gave very high yield of 77% in 1.3 h in conjunction with Nibpy₃Cl₂ as co-catalyst.

The Bedford PdCycle also gave high yield of 76% with co-catalyst Nien₃Cl₂ though in 10.1 h. Reaction catalyzed by the acetophenone oxime Pd cycle and NiCl₂(PPh₃)₂ also was fast, being complete in 3.30 h but with 58% yield. These reactions were not optimized. We then chose Ni[P(OPh)₃]₄ as the co-catalyst for exploring the reactions of various substituted aryl bromides.

We have earlier reported the catalysis of the Mizoroki-Heck reaction by Ni[P(OPh)₃]₄ and CuI separately [8]. The mixed metal catalysed reactions were complete in 2–6 h at 130–150 °C with yields ranging from 52 to 87%. The Table 2 is organized with comparison of the results of reactions of various aryl bromides and ethyl acrylate (EA) and

Table 2Ni–Pd catalyzedMizoroki-Heck reaction ofvarious aryl bromides

S. No.	Aryl bromide	Alkene	Catalyst A	Catalyst B	Time (h)	Yield (%)
1	C ₆ H ₅ Br	EA	Pd(OAc) ₂	NiCl ₂ (PPh ₃) ₂	2.15	85 ^a
2	C ₆ H ₅ Br	Styrene	Pd(OAc) ₂	Ni[P(OPh)3]4	8	67 ^a
3	4-CH ₃ OC ₆ H ₄ Br	EA	$Pd(OAc)_2$	Ni[P(OPh)3]4	5	70 ^a
4	4-CH ₃ O·C ₆ H ₄ Br	Styrene	$Pd(OAc)_2$	Ni[P(OPh) ₃] ₄	6	72 ^a
5	4-CH ₃ C ₆ H ₄ Br	EA	$Pd(OAc)_2$	Ni[P(OPh)3]4	4.15	67 ^a
6	4-CH ₃ C ₆ H ₄ Br	Styrene	Pd(OAc) ₂	Ni[P(OPh)3]4	4	52 ^a
7	4-Cl·C ₆ H ₄ Br	EA	$Pd(OAc)_2$	NiCl ₂ (PPh ₃) ₂	2.15	60 ^a
8	4-Cl·C ₆ H ₄ Br	EA	$Pd(OAc)_2$	Ni[P(OPh)3]4	2.20	60 ^a
9	4-Cl·C ₆ H ₄ Br	Styrene	$Pd(OAc)_2$	Ni[P(OPh)3]4	3.5	63 ^b
10	4-HO·C ₆ H ₄ Br	EA	Pd(OAc) ₂	NiCl ₂ (PPh ₃) ₂	6	65 ^a
11	4-HO·C ₆ H ₄ Br	Styrene	$Pd(OAc)_2$	Ni[P(OPh)3]4	7	75 ^c
12	4-HO·C ₆ H ₄ Br	EA	$Pd(OAc)_2$	Ni[P(OPh) ₃] ₄	5.3	65 ^c
13	1-Nap·Br	EA	Pd(OAc) ₂	NiCl ₂ (PPh ₃) ₂	4.5	69 ^a
14	1-Nap·Br	Styrene	Pd(OAc) ₂	Ni[P(OPh)3]4	2.1	57 ^a
15	4-C ₆ H ₅ C ₆ H ₄ ·Br	Styrene	$Pd(OAc)_2$	Ni[P(OPh)3]4	6	69 ^a
16	4-C ₆ H ₅ C ₆ H ₄ ·Br	EA	$Pd(OAc)_2$	Ni[P(OPh) ₃] ₄	3	87 ^b
17	2-CHO·C ₆ H ₄ ·Br	Styrene	$Pd(OAc)_2$	Ni[P(OPh) ₃] ₄	2	80 ^b

Reaction conditions: ArBr 1 mmol, Alkene 1–1.5 Eq, Base: 1.2 mmol, TBABr–1 mmol, NMP–5 mL, Pd(OAc)₂–2.5 mol %, [Ni]–5 mol %, 130–150 °C

EA ethyl acrylate

Base: ^aK₂CO₃, ^bCy₂NMe, ^cCs₂CO₃

styrene. A few examples were tried with $Pd(OAc)_2$ (cat) and $NiCl_2(PPh_3)_2$ co-catalyst, for comparison, which gave high yield of 85% with bromo benzene and ethyl acrylate in 2.15 h. While K_2CO_3 was the base of choice, 4-bromo phenol gave better results with Cs_2CO_3 as base. Cy_2NMe (N,N-Dicyclohexylmethylamine) was also an effective base for some of the reactions. Highest yield of 87% was obtained from 4-bromobiphenyl and ethyl acrylate in 3 h, catalysed by $Pd(OAc)_2$ and $Ni\{P(OPh)_3]_4$. CuI as a co-catalyst did not activate the reaction of 4-bromo anisole with ethyl acrylate or styrene.

The reactions were also energized by visible light giving very high yields and which results will be reported elsewhere. The Suzuki coupling of aryl bromides was also investigated with the Pd–Ni bimetallic catalysts (Scheme 3; Table 3). The reactions were carried out in a part aqueous solvent system of dioxane: water (1:1) without any surfactants, with the bimetallic Pd(OAc)₂ and [Ni] catalysts. The highest yield of 93% was obtained in the shortest time of 2 h in the reaction of 4-chlorobromobenzene with phenyl boronic acid catalyzed by $Pd(OAc)_2$ and $NiCl_2(PPh_3)_2$. All the Ni complexes tried, $Ni[P(OPh)_3]_4$, $NiCl_2(PPh_3)_2$, $Ni[DMG]_2$, NiSalen, $Nien_3Cl_2$, $Nibpy_3Cl_2$, $Ni-[8-HQ]_2$ were synergistically fast with $Pd(OAc)_2$, giving very high yields of 82–93% and in short reaction times of 2–6 h. A variety of aryl bromides reacted with different aryl boronic acids and all gave high yields showing generality.

The formation of Pd–Ni bimetallic nano clusters has been reported to be the active catalyst form in similar reactions demonstrated by Reetz and Chakraborti though their system is slightly different from the reaction conditions used by us [58, 59]. We believe that a homogeneous catalysis mechanism is in operation here though some complexes might be proceeding via partly nano particle catalysis. The catalysts used are homogeneous and visual observations do not show any colloidal particles in the reaction mixture thus confirming a homogeneous catalysis.



S. No.	Aryl bromides	Aryl boronic acid	[Ni] Co-catalyst	Product	Time (h)	Yield (%)
1	4-CH ₃ ·C ₆ H₄Br	C ₆ H ₅ B(OH) ₂	Ni[P(OPh) ₃] ₄	$4-CH_3 \cdot C_6H_4 \cdot C_6H_5$	4.5	90
2	4-Cl·C ₆ H ₄ Br	C ₆ H ₅ B(OH) ₂	NiCl ₂ (PPh ₃) ₂	$4-Cl\cdot C_6H_4\cdot C_6H_5$	2	93
3	4-CH ₃ ·C ₆ H ₄ Br	4-ClC ₆ H ₄ B(OH) ₂	Ni[DMG] ₂	$4-CH_3 \cdot C_6H_4 \cdot C_6H_4 - Cl$	3	82
4	4-CH ₃ O·C ₆ H ₄ ·Br	C ₆ H ₅ B(OH) ₂	NiSalen	$4-CH_3O-C_6H_4-C_6H_5$	6	88
5	1-Nap·Br	1-Nap·B(OH) ₂	Nien ₃ Cl ₂	1,1'-Binaphthalene	2.5	92
6	4-C ₆ H ₅ ·C ₆ H ₄ Br	2-NapB(OH) ₂	Nibpy ₃ Cl ₂	2-Nap-C ₆ H ₄ -4-C ₆ H ₅	4.2	89
7	$4-CH_3O \cdot C_6H_4 \cdot Br$	$1-\text{Nap} \cdot \text{B(OH)}_2$	Ni-[8-HQ] ₂	4-CH ₃ O·C ₆ H ₄ Nap-1	2.5	90

Table 3 Pd–Ni Bimetallic catalysis of the Suzuki coupling of aryl bromides

Reaction conditions: ArBr (0.5 mmol), Aryl boronic acid (0.6 mmol), K_3PO_4 (0.6 mmol), TBABr (0.5 mmol), Pd Cat (2.5 mol %), Ni Cat (5 mol %) Dioxane:Water (1:1. 10 ml), Argon, 130 °C

The mechanism of the catalysis could be explained thus; electron transfer occurs from Ni complex or salts to Pd (II) increasing the electron density on Pd reducing it to Pd(0), thus making it more nucleophilic which activates the oxidative addition to aryl bromides. This is then followed by the standard protocol catalytic cycle for the Mizoroki-Heck reaction and Suzuki coupling. Further studies are underway to confirm the nature of this bimetallic catalysis and will be the subject of a full paper.

4 Conclusions

We have thus demonstrated a convenient bimetallic Ni-Pd catalyst protocol for the Mizoroki-Heck reaction and the Suzuki coupling of aryl bromides. The reactions proceed in convenient short times giving high yields. The Mizoroki-Heck reaction retains the E-selectivity. The mixture of Ni[P(OPh)₃]₄ and Pd(OAc)₂ is an effective combination for the desired fast reactions of Mizoroki-Heck and Suzuki coupling while NiCl₂(PPh₃)₂ and Pd(OAc)₂ is comparable in activity and provides high yields. Further studies are underway to elucidate the mechanism. Most probably a redox mechanism is proceeding with a transfer of electrons from Ni to Pd under thermal conditions. This facilitates the formation of Pd (0) which then undergoes the wellestablished oxidative addition-reductive elimination protocol as understood for the Mizoroki-Heck reaction and the Suzuki-Miyaura coupling.

Acknowledgements Financial support from the CSIR Network Project, ORIGIN—under XII Five year plan CSC 0108 and PA-II post to VPP is gratefully acknowledged.

Compliance with Ethical Standards

Conflict of interest There are no conflicts to declare.

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