A Robust, Moisture- and Air-Stable Phosphine Mono-Ylide Palladacycle Precatalyst: A Simple and Highly Efficient System for Mizoroki–Heck Reactions

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Abstract: A palladacycle phosphine mono-ylide complex was identified as an efficient catalyst system for the Mizoroki–Heck cross-coupling reactions of aromatic or aliphatic olefins with a variety of aryl bromides and chlorides, including those containing electron-donating or electron-withdrawing substituents. The reactions, which proceeded in moderate to excellent yields, required relatively low loadings of palladium (10 ppm) and were performed under aerobic conditions. High catalyst activities with turnover frequencies of up to 20,000 h^{-1} were observed at 130 °C.

Key words: olefination, catalysis, palladium, ylides, Heck reaction

The palladium-catalyzed arylation of olefins, known as the Heck cross-coupling reaction, is one of the most versatile tools for forming carbon-carbon bonds.¹⁻⁶ Tolerance to a wide spectrum of functional groups in both substrates makes this reaction very useful in total syntheses. Historically, palladium complexes with phosphine ligands have been widely used to catalyze these reactions.7-10 The phosphine ligands act as stabilizers for catalytically active palladium(0) complexes that are generated in situ. Palladium complexes with bulky and strongly electrondonating trialkylphosphines are favored for carboncarbon coupling of aryl halides with styrene;11,12 however, diphosphine ligands, because of their chelating effects, generally shows better coordination ability in stabilizing active palladium species in the catalytic cycle. Among the existing catalysts for these reactions, the most effective are homogeneous palladium-ligand systems.¹³⁻¹⁹ The efficiency of a Heck reactions is greatly dependent on the reactivity of the palladacycle catalyst precursors. It is well established that palladacycle complexes containing phosphine ligands that combine both good donor strength and π -accepting capacity have high catalytic activities in Heck cross-coupling reactions.^{20–22} Over the past ten years, we have studied phosphorus ylides and their palladium complexes,^{23–28} and we have used some of these complexes in carbon-carbon coupling reactions.²⁹⁻³⁰ Here, we describe the use of precatalyst 1 to promote the Mizoroki-Heck coupling reaction of aryl bromides or chlorides with olefins (Scheme 1). The reaction proceeds smoothly with deactivated aryl bromides or activated aryl chlorides and it

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gives good yields at low palladium loadings under aerobic conditions.

The catalyst precursor **1** used for the Mizoroki–Heck cross-coupling reaction was prepared in high yield by reaction of 1-biphenyl-4-yl-2-[[(diphenylphosphino)-methyl](phenyl)phosphino]ethanone with dichloro(cyclo-octadienyl)palladium in a 1:1 molar ratio at room temperature.³¹

The palladium-catalyzed Mizoroki–Heck reaction is among the most important carbon–carbon bond-forming processes for the vinylation of aryl or vinyl halides. As a result, considerable effort has been made to develop new and improved protocols for the Heck coupling reaction since the pivotal discovery of the reaction by Heck and Mizoroki in the early 1970s.^{32–35}

Many palladium phosphine complexes have been used as catalyst in these reactions,^{36,37} but most suffer from problems such as a need for a high palladium loading, low yields from less-active aryl bromides, instability toward air and moisture, and the generation of quantities of 1,1-diphenylethene as a byproduct.³⁸ With these precedents in mind, and encouraged by our earlier work,^{29,30,37,39,40} we decided to explore the scope and limitations of various substrates, as well as the efficiency of our precatalyst.

First, to optimize the reaction conditions, we examined the model reactions of 4-bromobenzaldehyde with styrene and with ethyl acrylate (Table 1). A control experiment indicated that coupling did not proceed in the absence of a catalyst (entry 1), and a catalyst loading of 10 ppm was found to be optimal [entry 5; R = Ph (81%), CO₂Et (85%)].



Scheme 1 Mizoroki–Heck cross-coupling reaction using a phosphine mono-ylide palladacycle as the precatalyst

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Next, we examined the effects of several solvents. Polar solvents such as *N*,*N*-dimethylformamide, *N*-methylpyrrolidin-2-one, or methanol gave acceptable yields (entries 5, 10, and 11), whereas nonpolar solvents such as toluene and 1,4-dioxane gave low to moderate yields of 40 and 65%, respectively (entries 12 and 13). The reaction did not proceed in water; no product was observed, even when the reaction was extended to 48 hours (entry 14). Only a trace of product was detectable under solvent-free conditions with triethylamine as base (entry 20).

Having selecting N,N-dimethylformamide as the optimal solvent, we investigated the effects of various bases on the reaction. It was clear that inorganic bases (Table 1 entries 5 and 15–17) were much better than organic ones (entries

18 and 19). Among the inorganic bases tested, potassium carbonate proved to be the most efficient and gave a good isolated yield (entry 5). On successively increasing the temperature from 60 °C to 100, 130, and 180 °C, the reactivity of the palladacycle increased, resulting in yields of 44, 70, 81, and 80%, respectively (entries 4–7; R = Ph). Therefore, 10 ppm of the palladacycle with *N*,*N*-dimeth-ylformamide as solvent and potassium carbonate as the base at 130 °C (entry 5) were chosen as the optimal conditions for the reaction.

Next, we studied the application of these conditions to reactions of styrene with various aryl bromides and chlorides, and the results are summarized in Table 2. In most cases, products were obtained in very good to excellent

Table 1 Mizoroki-Heck Coupling: Optimization of the Reaction Con	nditions
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Entry ^a	Catalyst (ppm)	Solvent	Base	Temp (°C)	Yield ^b (%)	
					$\mathbf{R} = \mathbf{P}\mathbf{h}$	$R = CO_2Et$
1	-	DMF	K ₂ CO ₃	130	_	_
2	1000	DMF	K ₂ CO ₃	130	83	85
3	100	DMF	K ₂ CO ₃	130	80	84
4	10	DMF	K ₂ CO ₃	180	83	86
5	10	DMF	K ₂ CO ₃	130	81	85
6	10	DMF	K ₂ CO ₃	100	70	80
7	10	DMF	K ₂ CO ₃	60	44	56
8	50	DMF	K ₂ CO ₃	130	81	85
9	5	DMF	K ₂ CO ₃	130	56	63
10	10	NMP	K ₂ CO ₃	130	72	75
11	10	МеОН	K ₂ CO ₃	60	62	65
12	10	toluene	K ₂ CO ₃	100	40	43
13	10	1,4-dioxane	K ₂ CO ₃	80	48	52
14°	10	H ₂ O	K ₂ CO ₃	100	_	_
15	10	DMF	Na ₂ CO ₃	130	72	76
16	10	DMF	Cs ₂ CO ₃	130	73	79
17	10	DMF	NaF	130	68	65
18	10	DMF	NaOAc	130	70	70
19	10	DMF	Et ₃ N	130	47	48
20	10	-	Et ₃ N	90	trace	trace
21	10	DMF	_	130	trace	trace

^a Reaction conditions: 4-BrC₆H₄CHO (1 mmol), olefin (2 mmol), base (1.5 mmol), solvent (3 mL), palladacycle catalyst (5–1000 ppm), 24 h, under air.

^b Isolated yield.

^c Reaction extended to 48 h.

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 Table 2
 Mizoroki–Heck Cross-Coupling Reactions of Aryl Halides

 with Styrene
 Image: Mizoroki–Heck Cross-Coupling Reactions of Aryl Halides

ArX	+	catalyst (10 pp	om) Ar-		>
				1a–7a	
Entry ^a	Х	Ar	Yield ^b (%)	TON°	$\begin{array}{c} TOF^d\\ (h^{-1}) \end{array}$
1	Br	Ph	76.5	76500	3180
2	Br	4-Tol	70.2	70200	2920
3	Br	4-MeCOC ₆ H ₄	80.0	80000	3330
4	Br	$4\text{-HCOC}_6\text{H}_4$	48.1	48100	2000
5	Br	$4-O_2NC_6H_4$	79.2	79200	3300
6	Br	2-thienyl	69.3	69300	2880
7	Br	1-naphthyl	75.4	75400	3140
8	Cl	Ph	62.0 (70.1) ^f	62000 (70100)	2580 (2920)
9	Cl	4-Tol	51.1 (62.0) ^f	51100 (62000)	2120 (2580)
10	Cl	4-MeCOC ₆ H ₄	60.0 (73.2) ^f	60000 (73200)	2500 (3050)

^a Reaction conditions: aryl halide (1 mmol), styrene (2 mmol), K₂CO₃ (1.5 mmol), DMF (3 mL), catalyst (10 ppm), 24 h, 130 °C.

^b Isolated yield.

^c TON = (moles of product)/(moles of catalyst).

^d TOF = TON/time (h).

^f The reaction was carried out under reflux at 180 °C.

yields and >99% *trans* selectivity. Under the optimized reaction conditions, both electron-deficient and electron-rich aryl bromides coupled cleanly in good to excellent yields (entries 2–5). Coupling of activated aryl bromides with styrene proceeded in excellent yields (entries 3–5), and even bromobenzene, an electronically neutral substrate, coupled in excellent yield (entry 1). A nonactivated aryl bromide bearing a methyl group coupled with styrene in good yield (entry 2), and good reactivities were also observed for coupling reactions of styrene with 1-bromonaphthalene and with 2-bromothiophene (Table 2, entries 6 and 7).

Various aryl chlorides were also found to couple with styrene under similar conditions, although their reactivities were lower than those of their bromo counterparts. An electronically neutral aryl chloride gave a moderate yield (entry 8). The efficiency of the robust palladacycle catalysts for coupling of aryl chlorides with olefins in Mizoroki-Heck reactions commonly increases when the reaction temperature is above 180 °C, as occurred in entries 8-10, but this is frequently associated with oxidation of the phosphorus ligand.^{41,42} With the electron-rich 4-chlorotoluene, the yield was moderate (entry 9), and the electrondeficient substrate 4-chloroacetophenone coupled similarly (entry 10). These observations are in keeping with the fact that oxidative addition reactions of aryl chlorides occur less readily than do those of aryl bromides.12,21,37,39,40

To extend the scope of this catalytic system, we examined the coupling reactions of various aryl bromides and chlorides with ethyl acrylate under the same optimized conditions, and the results are presented in Table 3. In general, all the aryl halides gave the corresponding products (1b– 7b) in moderate to good yields of 51% to 88% in the presence of 10 ppm of the palladium catalyst.

 Table 3
 Mizoroki–Heck Cross-Coupling Reactions of Aryl Halides with Ethyl Acrylate (Abschnitt 1 von 2)

Entry ^a	ArX	Product	Time (h)	Yield (%) ^b	TON	TOF (h ⁻¹)
1	PhBr	OEt	24	86	86400	3600
2	4-TolBr	1b OEt H ₃ C	29	68	67800	2330
3	4-MeCOC₀H₄Br	OEt CH ₃	4	81	81000	20250

Entry ^a	ArX	Product	Time (h)	Yield (%) ^b	TON	TOF (h^{-1})
4	4-HCOC ₆ H₄Br	OEt H 4b	4	76	75700	18920
5	4-O ₂ NC ₆ H ₄ Br	O ₂ N OEt	4	72	72000	18000
6	Br		24	82	81600	3400
7	Br	ob OEt 7b	17	88	88400	5200
8	PhCl	OEt 1b	24	63 (74)°	63100 (74200)	2620 (3090)
9	4-TolCl	H ₃ C OEt	24	51 (63)°	51000 (63000)	2125 (2625)
10	4-MeCOC ₆ H ₄ Cl	OCH3	24	69 (79)°	69000 (79000)	2870 (3290)
		3b				

Table 3	Mizoroki–Heck (Cross-Coupling	Reactions of Ary	l Halides with Ethy	Acrylate	(Abschnitt 2 von 2	2) (continued)
I able 5	WILLOIOKI TICCK C	Joss Coupling	icedetions of ring	i manaes with Duny	i i i i i i i i i i i i i i i i i i i	(11050mmtt 2 von 2	2) (commuted)

^a Reaction conditions: aryl halide (1 mmol), ethyl acrylate (2 mmol), K₂CO₃ (1.5 mmol), DMF (3 mL), catalyst (10 ppm), 130 °C.

^b Isolated yield.

° The reaction was carried out under reflux at 180 °C.

Although several catalytic systems have been reported to support Mizoroki–Heck cross-coupling reactions, phosphine mono-ylide palladacycles of the type exemplified by **1** are novel with respect to the P and CH phosphorus ylide environment. The electronic and steric nature of the ligand and the coordination number of palladium significantly affect the oxidative addition and reductive elimination steps.⁴³

A comparison of phosphine mono-ylide palladacycle **1** with other catalytic systems in Mizoroki–Heck reactions is presented in Table 4. Satisfactory results for the cou-

pling of styrene and ethyl acrylate with aryl halides were achieved with conventional palladium catalysts such as di-(η^3 -allyl)dichlorodipalladium,⁴⁴ palladium(II) acetate,⁴⁵ and palladium(II) acetate with 6 mol% of Dave-Phos⁶ (entries 1–3 and 6), as well as with N-heterocyclic carbene palladium complex⁴⁶ (entries 4 and 5), a phosphane palladacycle⁴⁷ (entry 7), palladacycles modified with C,N and C,S chelate ligands^{48,52} (entries 8 and 12), P,C and P,P chelate palladacycles³⁹ (entries 13 and 14), cyclopalladated ferrocenylimines⁴⁹ (entry 10). Table 4 shows that palladacycle catalyst 1 (entries 15 and 16) gives superior yields with lower catalyst loadings under aerobic conditions in comparison with similar catalytic systems (entries 4–7, 10, and 12). Finally, we compared catalyst 1 with our previous catalysts (entries 13 and 14) to examine the relationships between the reaction rates and the structures of the palladacycles and the presence bulky phosphine ligands. As can be seen in Table 4, the steric hindrance and coordination number in palladacycle 1 affects the oxidative addition and reductive elimination steps⁴³ and, as expected, the reaction is significantly slower. In conclusion, we have developed an efficient and new catalyst precursor for the Mizoroki–Heck cross-coupling reaction. In the presence of complex 1 as precatalyst, various aryl bromides, including those with electron-donating or electron-withdrawing substituents, coupled effectively to give the corresponding products in moderate to excellent yield as *trans*-isomers. Further studies on the applicability of this system to other organic transformations are currently under way.

Table 4Comparison of Catalytic Activities of Various Palladium Complexes that Promote the Mizoroki–Heck Coupling of Olefins with ArylHalides

$x \longrightarrow R^1 + R^2 \longrightarrow R^1 - R^2$									
Entry	ArX	Catalyst ^a	[Pd] (ppm)	Base	Solvent	Temp (°C)	Time (h)	Yield (%) $R^2 = Ph$	$R^2 = CO_2Et$
1 ^b	PhBr	[Pd1] ⁴⁴	_c	Na ₂ CO ₃	DMA	120	24	87	_
2	PhI	[Pd2] ⁴⁵	10	Et ₃ N	IL^d	100	4	86	94 ^e
3	$4-O_2NC_6H_4Br$	[Pd2] ⁴⁵	10	Et ₃ N	IL	100	24	-	48
4	PhBr	[Pd3] ⁴⁶	12,000	NaOAc	DMF	140	3	100	_
5	PhBr	[Pd3] ⁴⁶	12,000	NaOAc	H_2O	140	24	100	_
6	4-HCOC ₆ H ₄ Cl	[Pd4] ⁶	20,000	Bu ₄ NAc	1,4-dioxane	80	24	92	89
7	PhCl	[Pd5] ⁴⁷	10,000	K ₃ PO ₄	DMF-H ₂ O	85	8	82 ^f	94
8	PhBr	[Pd6] ⁴⁸	0.5	K ₂ CO ₃	NMP	150	34	86.6 ^g	90
9	PhI	[Pd7] ⁴⁹	3.27	Et ₃ N	1,4-dioxane	100	8	38.2	98.7 ^h
10	PhI	[Pd8] ⁵⁰	2000	Bu ₃ N	DMA	100	24	64	96 ⁱ
11 ^j	PhBr	[Pd9] ⁵¹	100	K_3PO_4	DMF	140	24	91	99 ^k
12	PhBr	[Pd10] ⁵²	5000	Et ₃ N	DMA	120	15	86	_
13	PhBr	[Pd11] ³⁹	10	Cs ₂ CO ₃	NMP	130	4	74 ¹	73
14	4-TolCl	[Pd12] ³⁹	10	K ₂ CO ₃	DMF	130	4	45	46
15	PhBr	[Pd13] ^m	10	K ₂ CO ₃	DMF	130	24	76.5	86.4
16	PhCl	[Pd13] ^m	10	K ₂ CO ₃	DMF	130	24	62.0	71.1

^a [Pd1]: [Pd(η^3 -All)Cl]₂; [Pd2]: Pd(OAc)₂; [Pd3]: N-heterocyclic carbene Pd complex; [Pd4]: Pd(OAc)₂ + (6 mol% of Dave-Phos); [Pd5]: β -diketiminatophosphane Pd complex; [Pd6]: di-3-chlorobis(dimethylbenzylamine-6-*C*,*N*)dipalladium(II); [Pd7]: Cyclopalladated ferrocenylimines; [Pd8]: Palladium catalyst supported on a commercial synthetic adsorbent, DIAION HP20; [Pd9]: [PdCl{[(η^5 -C₅H₅)]Fe[(η^5 -C₅H₃)C(CH₃)=]NC₁₂H₂₅]}₂ (cyclopalladated ferrocenylimines); [Pd10]: Furancarbothioamide-based palladacycle; [Pd11]: [(P^P)Pd(P^C)](OTf₂; [Pd12]: [Pd(dppe)(OTf)₂]; [Pd13]: **1** (this work).

^b Using 0.75 mmol of TBAB.

^c [ArX]/[Pd] = 10000.

^d Ionic Liquid [(HQ-PEG₁₀₀₀-DIL)(BF₄)].

^e Reaction time 2 h.

^f Reaction time 10 h with C₄H₃SCl as starting material.

^g Reaction time 29 h.

^h Reaction time 2.5 h.

ⁱ Reaction time 4 h.

^j TBAB co-catalyst.

^k Reaction time 12 h.

- ¹K₂CO₃ and DMF.
- ^m This work.

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1-Biphenyl-4-yl-2-[[(diphenylphosphino)methyl](phenyl)phosphino]ethanone

(Ph₂P)₂CH₂ (0.50 g, 1.30 mmol) was dissolved in CHCl₃ (8 mL), and a solution of 1-(3-bromobiphenyl-4-yl)ethanone (0.36 g, 1.30 mmol) in CHCl₃ (4 mL) was added dropwise. The mixture was stirred for 15 h at r.t. then concentrated to about 2 mL under reduced pressure. Et₂O (2 × 10 mL) was added and the phosphonium salt was collected by filtration and dried under reduced pressure. The salt (0.33 g, 0.50 mmol) was treated with a solution of Et₃N (0.50 mL) in toluene (15 mL), and the Et₃N ·HBr was filtered off. Concentration of the toluene layer to about 1 mL and subsequent addition of Et₃N (25 mL) precipitated a white solid; yield: 0.21 g (71%); mp 144–146 °C. IR (KBr): 1565 cm⁻¹ (v_{C=O}). ¹H NMR (89.60 MHz, CDCl₃): δ = 3.70 (d, ²J_{PH} = 14.22, 2 H, CH₂), 4.36 (br s, 1 H, CH), 7.27–8.02 (m, 29 H, Ph). ³¹P NMR (36.26 MHz, CDCl₃): δ = -29.78 (d, ²J_{PP} = 63.67, PPh₂), 11.32 (d, ²J_{PP} = 63.24, PCH). ¹³C NMR (100.62 MHz, CDCl₃): δ = 24.52 (dd, ¹J_{PC} = 57.64, 32.28, PCH₂P), 49.94 (d, ¹J_{PC} = 114.46, CH), 124.89–141.84 (m, Ph), 184.60 (s, CO). Anal. Calcd. for C₃₉H₃₂OP₂: C, 80.95; H, 5.57. Found: C, 80.86; H, 5.56.

Mizoroki–Heck Reaction of Aryl Halides with Olefins; General Procedure

A mixture of the aryl halide (1 mmol), olefin (2 mmol), palladacycle catalyst 1 (10 ppm), K_2CO_3 (1.5 mmol), and DMF (3 mL) was heated to 130 °C. The mixture was then cooled to r.t. and the solvent was removed under reduced pressure. The mixture was diluted with hexane (15 mL), and H_2O (15 mL) was added. The organic layer was separated, washed with brine (15 mL), dried (CaCl₂), and concentrated under reduced pressure. Liquid products were purified by column chromatography [silica gel, hexane–EtOAc (80:20)], whereas solids were purified by crystallization (EtOH–H₂O) or by slow evaporation of a solution in hexane. Products were identified by comparison of their FTIR and ¹H and ¹³C NMR spectra with those reported in the literature.^{39,52,54–69}

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