Cryptand-22 as an Efficient Ligand for the Palladium-Catalyzed Mizoroki– Heck Reaction under Air

Barahman Movassagh,* Shahriar Yasham, Mozhgan Navidi

Department of Chemistry, K. N. Toosi University of Technology, P.O. Box 16315-1618, Tehran, Iran Fax +98(21)22853650; E-mail: bmovass1178@yahoo.com Received: 06.08.2013; Accepted after revision: 05.09.2013

Abstract: An efficient catalytic system for the Mizoroki–Heck cross-coupling reaction was developed based on the air- and heat-stable palladium(II) chloride–cryptand 22 complex. The complex is a highly active catalyst for coupling of aryl iodides, bromides, or chlorides with various olefins.

Key words: Heck reaction, cross-coupling, halides, olefins, cryptands, catalysis

Palladium-catalyzed cross-coupling reactions between aryl halides and terminal acetylenes (commonly referred to as the Mizoroki-Heck reaction) is a versatile, powerful, and popular tool for the synthesis of various substituted olefins, dienes, and precursors of conjugated polymers.¹ This reaction has also been used in syntheses of natural products² and pharmaceuticals.³ Unlike other carbon-carbon bond-forming reactions that involve a polar addition, the Mizoroki-Heck reaction can be performed in the presence of sensitive functional groups such as aldehyde, ketone, cyano, amino, hydroxy, carboxy, ester, or nitro groups.⁴ The conventional Mizoroki-Heck reaction is typically performed with 1-5 mol% of a palladium catalyst together with a phosphine⁵ or phosphorus⁶ ligand in the presence of a suitable base. However, phosphine ligands are toxic, expensive, nonrecoverable, and unstable at high temperatures, so the development of a phosphinefree palladium catalyst is a topic of enormous interest. Moreover, the Mizoroki-Heck reaction retains some limitations, especially in relation to the use of certain reagents. In particular, a major restriction on palladiumcatalyzed coupling processes has been the poor reactivity of cheaper and more readily available aryl chlorides and bromides in comparison with more active aryl iodides. Therefore, the search for efficient catalysts for the crosscoupling of olefins with deactivated aryl bromides and, eventually, activated aryl chloride is under way. Recently, selenium-⁷ and nitrogen-based⁸ catalysts, sulfur-based palladacycles,⁹ and N-heterocyclic carbene ligands¹⁰ have also been introduced as catalyst systems for the Mizoroki-Heck reaction, with an emphasis on air- and heat-stable palladium catalysts; however, these non-phosphine ligands are not commercially available, and some require laborious and cumbersome preparation.

SYNLETT 2013, 24, 000A–000D Advanced online publication: 24.10.2013 DOI: 10.1055/s-0033-1339897; Art ID: ST-2013-D0755-L © Georg Thieme Verlag Stuttgart · New York In cross-coupling reactions, amines are generally used as bases, but they can also serve to stabilize the reactive palladium intermediates.¹¹ Because of their stronger σ-donation, which favors both the oxidative addition step and the slow reductive elimination step in the catalytic cycle, ligands of the N.N-type show superior properties to P.Ptype ligands in terms of both palladium complexation and catalysis of cross-coupling reactions.¹² Very recently, as part of our attempts to identify a robust and easily prepared system to catalyze carbon-carbon bond-forming reactions of terminal alkynes with acyl halides, we demonstrated that the complex of palladium(II) chloride with the commercially available diazacrown ether cryptand 22 (1,4,10,13-tetraoxa-7,16-diazacyclooctadecane) operates as an active homogeneous catalyst under aerobic conditions.¹³ With some modifications, this catalyst can be readily prepared by the method described by Sun and co-workers.¹⁴ The remarkable chelating effect of the N- and O-containing cryptand ligand, together with its flexibility, facilitate stabilization of reactive palladium intermediates¹¹ and suppress the formation of palladium black, even at high temperatures under air. The Fouriertransform IR spectrum of the complex shows a v_{N-H} stretch at 3224 cm⁻¹, a lower frequency than observed for the free ligand (3327 cm⁻¹), indicating coordination between the cryptand nitrogen atoms and the palladium(II) ion.

Here, we introduce the homogeneous air- and heat-stable palladium(II) chloride-cryptand 22 complex (PdCl₂-C22), as a highly efficient catalytic system for performing the Mizoroki-Heck reaction without using phosphoruscontaining ligands. A literature survey revealed that reaction conditions, such as the base, solvent, and reaction temperature, have marked effects on this reaction. We began our investigation by attempting to optimize the conditions for the cross-coupling reaction. We therefore chose iodobenzene and styrene as coupling partners, and we examined their reaction in the presence of the palladium(II) chloride-cryptand 22 complex (0.9 mol%) under various aerobic conditions (Table 1). The reaction rates were markedly dependent on the base, solvent, and temperature, as well as the concentration of the palladium complex. Various organic and inorganic bases were screened, as the role of the base is to neutralize and remove hydrogen iodide. The yield of the cross-coupling product was reduced when inorganic bases such as potassium carbonate, sodium carbonate, or potassium tert-butoxide were used (Table 1, entries 13-15). Moreover, a considerable

increase in yield was observed in the presence of organic bases, such as triethylamine, in N,N-dimethylformamide at a high temperature. Several other solvents, including tetrahydrofuran, N-methylpyrrolidin-2-one, dimethylacetamide, and dimethyl sulfoxide were also surveyed under similar conditions, but compared with N,Ndimethylformamide, all gave inferior results (entries 1-4). Also, low palladium concentrations gave decreased yields (entries 6 and 7). An increase in the catalyst concentration to 1.1 mol% did not have any significant effect on the yield (entry 8). We concluded that the optimal conditions for the coupling reaction involve the use of triethylamine as the base in N,N-dimethylformamide at $130 \,^{\circ}$ C in the presence of 0.9 mol% of the catalyst. Under these conditions, trans-stilbene was obtained in 97% yield after 15 minutes (entry 11).

Table 1 Screening of Reaction Conditions



Entry ^a	Solvent	Catalyst (mol%)	Temp (°C)	Base	Time (h)	Yield ^b (%)
1	THF	0.9	115	Et ₃ N	6	31
2	DMSO	0.9	115	Et ₃ N	1.5	84
3	NMP	0.9	115	Et ₃ N	3	63
4	DMAc ^c	0.9	115	Et ₃ N	2	60
5	DMF	0.9	115	Et ₃ N	1.5	87
6	DMF	0.7	115	Et ₃ N	2.75	80
7	DMF	0.5	115	Et ₃ N	4	71
8	DMF	1.1	115	Et ₃ N	1	89
9	DMF	0.9	100	Et ₃ N	2	84
10	DMF	0.9	60	Et ₃ N	4	37
11	DMF	0.9	130	Et ₃ N	0.25	97
12	DMF	0.9	130	DIPEA	1.5	77
13	DMF	0.9	130	K ₂ CO ₃	4.5	68
14	DMF	0.9	130	Na ₂ CO ₃	7	64
15	DMF	0.9	130	t-BuOK	1	61

^a Reaction conditions: PhI (1 mmol), styrene (1.1 mmol), base (1.1 mmol), solvent (1 mL), under air.

^b Isolated yield.

^c DMAc = *N*,*N*-dimethylacetamide.

Having identified the optimal reaction conditions, we extended the scope of the method to include the coupling reactions of activated, nonactivated, or deactivated aryl halides 1 with various vinylic substrates 2 (styrene, 4-methoxystyrene, butyl acrylate, and acrylamide) in N,N-dimethylformamide/triethylamine at 130 °C in the presence of 0.9 mol% of the catalyst (Table 2).¹⁵

Table 2 Palladium(II) Chloride–Cryptand 22-Catalyzed Mizoroki–Heck Coupling of Aryl Halides with Olefins^a

ArV .		-C22 Ar	<u> </u>		
1	B DMF, Et ₃ l	N, 130 °C	3 R		
Entry	ArX	R	Product	Time (h)	Yield ^{b,c} (%)
1	PhI	Ph	3a	0.25	97 ^{8a}
2	PhI	4-MeOC ₆ H ₄	3b	0.75	80 ^{10b}
3	PhI	CONH ₂	3c	2	8416
4	PhI	CO ₂ Bu	3d	1	91 ^{8a}
5	$4-MeC_6H_4I$	Ph	3e	1	90 ^{2a}
6	2-MeC ₆ H ₄ I	Ph	3f	3	7217
7	$4-MeOC_6H_4I$	Ph	3g	1	8018
8	1-iodonapthalene	Ph	3h	1.5	8219
9	$4-MeC_6H_4I$	CO ₂ Bu	3i	1	92 ^{8a}
10	2-iodothiophene	CO ₂ Bu	3j	1	9420
11	PhBr	Ph	3k	48	16 ^{8a}
12	PhBr	Ph	$\mathbf{3k}^{d}$	4	73 ^{8a}
13	PhBr	CO ₂ Bu	31 ^d	3.5	69 ^{8a}
14	$4-O_2NC_6H_4Br$	Ph	$\mathbf{3m}^{d}$	2	85 ^{8a}
15	4-O ₂ NC ₆ H ₄ Br	CO ₂ Bu	3n ^d	3	81 ^{8a}
16	4-MeOC ₆ H ₄ Br	Ph	30 ^d	3.5	70 ^{10b}
17	4-MeOC ₆ H ₄ Br	CO ₂ Bu	3p ^d	4.5	62 ^{8a}
18	4-BrC ₆ H ₄ CN	Ph	$\mathbf{3q}^{d}$	3	8221
19	4-BrC ₆ H ₄ CHO	Ph	3r ^d	3	8522
20	PhCl	Ph	3s ^d	8	51 ^{8a}
21	4-MeCOC ₆ H ₄ Cl	Ph	3t ^d	5	6423
22	4-ClC ₆ H ₄ CN	Ph	$\mathbf{3u}^{d}$	4	66 ²⁴

^a Reaction conditions (unless otherwise indicated): aryl halide 1 (1 mmol), olefin 2 (1.1 mmol), Et_3N (1.1 mmol), $PdCl_2$ -cryptand 22 (0.9 mol%), DMF (1 mL), 130 °C, under air.

^b Isolated yield

^c References are given for known compounds.

^d TBAB (1 mmol) was added.

The *trans*-products were selectively obtained in all cases. The results show that the palladium(II) chloride–cryptand 22 catalytic system is remarkably active and tolerates a range of functional groups. As expected, the reaction of iodobenzene, 4-iodotoluene, 1-iodo-4-methoxybenzene, 1-iodonaphthalene, and 2-iodothiophene all proceeded very smoothly within 0.25 to 2 hours to give the desired products in 80–97% isolated yield (Table 2, entries 1–5, 7–10). However, the reaction of sterically hindered 2-io-dotoluene with styrene gave a lower yield (entry 6). Under these same reaction conditions, coupling of bromobenzene with styrene gave a very poor yield (16%) after 48 hours (entry 11); therefore, tetrabutylammonium bromide (1 equiv) was added to the reaction mixture for the cross-coupling of aryl bromides or chlorides with alkenes. Activated aryl bromides, such as 1-bromo-4-nitrobenzene, 4-bromobenzonitrile, and 4-bromobenzaldehyde, then coupled rapidly in high yields (entries 14, 15, 18, and 19).

We also investigated the Mizoroki–Heck cross-coupling of styrene with activated aryl chlorides, such as 4-chloroacetophenone and 4-chlorobenzonitrile, as well as nonactivated electron-neutral chlorobenzene under similar reaction conditions in the presence of tetrabutylammonium bromide (1 equiv) (entries 20–22). Compared with the corresponding bromo analogues, the reactions of the chloro derivatives gave moderate yields and required longer times.

In summary, the palladium chloride–cryptand 22 complex has been introduced as a potential catalyst for Mizoroki– Heck reactions of aryl halides with terminal olefins under phosphine-free conditions. This catalyst has the advantages of being thermally stable, readily synthesized, inexpensive, easily handled, and operating under air. Furthermore, cryptand-22 might act as a ligand in stabilizing the palladium(0) species in the Mizoroki–Heck reaction.

Acknowledgment

We thank the Research Council of K. N. Toosi University of Technology for financial support. The authors express their gratitude to Dr. Sogand Noroozizadeh for editing the English content of this manuscript.

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- (15) Aralkenes 3; General Procedure

A 5 mL round-bottomed flask was charged with aryl halide 1 (1 mmol), alkene 2 (1.1 mmol), PdCl₂–cryptand 22 (0.009 mmol, 0.9 mol%), Et₃N (1.1 mmol), and DMF (1 mL). [For aryl bromides or chlorides, TBAB (1 mmol) was also added]. The mixture was stirred at 130 °C for the appropriate time (Table 2) while the progress of the reaction was monitored (TLC). Upon completion of the reaction, the mixture was cooled to r.t., poured into H₂O (10 mL), and extracted with CH₂Cl₂ (3 × 8 mL). The combined organic extracts were washed with brine (2 × 8 mL), dried (MgSO₄), and concentrated. Purification by preparative TLC [silica gel, hexane or hexane–EtOAc (9:1)] gave the pure product. 1-Methyl-4-[(*E*)-2-phenylvinyl]]benzene (3e)

White solid; yield: 175 mg (90%); mp 119–122 °C (Lit.^{2a} 120–122 °C). ¹H NMR (300 MHz, CDCl₃): δ = 2.41 (s, 3 H), 7.13 (s, 2 H), 7.22 (d, *J* = 7.9 Hz, 2 H), 7.29 (t, *J* = 7.3 Hz, 1 H), 7.40 (t, *J* = 7.3 Hz, 2 H), 7.47 (d, *J* = 7.9 Hz, 2 H), 7.55 (d, *J* = 7.4 Hz, 2 H). ¹³C NMR (75 MHz, CDCl₃): δ = 21.3, 126.45, 126.49, 127.5, 127.7, 128.65, 128.7, 129.5, 134.6, 137.55, 137.57.

1-Methyl-2-[(E)-2-phenylvinyl]benzene (3f)

Pale-yellow oil; yield: 138 mg (72%). ¹H NMR (300 MHz, CDCl₃): δ = 2.51 (s, 3 H), 7.08 (d, *J* = 16.1 Hz, 1 H), 7.26–7.47 (m, 7 H), 7.61 (d, *J* = 7.6 Hz, 2 H), 7.68 (d, *J* = 6.5 Hz, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ = 20.0, 125.4, 126.3, 126.6, 126.7, 127.65, 127.69, 128.8, 130.1, 130.5, 135.9, 136.5, 137.8.

1-Methoxy-4-[(E)-2-phenylvinyl]benzene (3g)

С

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White solid; yield: 168 mg (80%); mp 136–137 °C (Lit.¹⁸ 135–137 °C). ¹H NMR (300 MHz, CDCl₃): δ = 3.85 (s, 3 H), 6.89–6.94 (m, 2 H), 6.99 (d, *J* = 16.3 Hz, 1 H), 7.09 (d, *J* = 16.3 Hz, 1 H), 7.23–7.28 (m, 1 H), 7.36 (t, *J* = 7.7 Hz, 2 H), 7.45–7.52 (m, 4 H). ¹³C NMR (75 MHz, CDCl₃): δ = 55.3, 114.1, 126.3, 126.6, 127.2, 127.7, 128.2, 128.7, 130.1, 137.7, 159.3.

Butyl (2*E*)-3-(4-Methoxyphenyl)acrylate (3i)

Colorless oil; yield: 200 mg (92%). ¹H NMR (300 MHz, CDCl₃): $\delta = 0.97$ (t, J = 7.3 Hz, 3 H), 1.43 (sext, J = 7.4 Hz, 2 H), 1.70 (quin, J = 6.6 Hz, 2 H), 2.34 (s, 3 H), 4.20 (t, J = 6.6 Hz, 2 H), 6.39 (d, J = 16.0 Hz, 1 H), 7.16 (d, J = 8.0 Hz, 2 H), 7.40 (d, J = 8.0 Hz, 2 H), 7.66 (d, J = 16.0 Hz, 1 H). ¹³C NMR (75 MHz, CDCl₃): $\delta = 13.8$, 19.2, 21.4, 30.8, 64.3, 117.2, 128.0, 129.6, 131.7, 140.5, 144.5, 167.2.

Butyl (2*E*)-3-(2-Thienyl)acrylate (3j)

Pale-yellow oil; yield: 197 mg (94%). ¹H NMR (300 MHz, CDCl₃): $\delta = 0.96$ (t, J = 7.3 Hz, 3 H), 1.43 (sext, J = 7.2 Hz, 2 H), 1.68 (quin, J = 6.8 Hz, 2 H), 4.19 (t, J = 6.6 Hz, 2 H), 6.24 (d, J = 15.7 Hz, 1 H), 7.04 (t, J = 4.9 Hz, 1 H), 7.24–7.27 (m, 1 H), 7.36 (d, J = 4.9 Hz, 1 H), 7.77 (d, J = 15.7 Hz, 1 H). ¹³C NMR (75 MHz, CDCl₃): $\delta = 13.8$, 19.2, 30.8, 64.4, 117.0, 128.1, 128.3, 130.8, 137.0, 139.6, 166.9.

4-[(*E*)-2-Phenylvinyl]benzonitrile (3q)

White solid; yield: 168 mg (82%); mp 115–118 °C (Lit.²¹ 116–118 °C). ¹H NMR (300 MHz, CDCl₃): δ = 7.09 (d, *J* = 16.3 Hz, 1 H), 7.23 (d, *J* = 16.3 Hz, 1 H), 7.26–7.42 (m, 3 H), 7.53–7.66 (m, 6 H). ¹³C NMR (75 MHz, CDCl₃): δ = 110.6, 119.1, 126.7, 126.88, 126.94, 128.7, 128.9, 132.4, 132.5, 136.3, 141.8.

4-[(*E*)-2-Phenylvinyl]benzaldehyde (3r)

Pale-yellow solid; yield: 176 mg (85%); mp 117-118 °C

(Lit.²² 115–116 °C). ¹H NMR (300 MHz, CDCl₃): δ = 7.15 (d, *J* = 16.3 Hz, 1 H), 7.28 (d, *J* = 16.3 Hz, 1 H), 7.32–7.42 (m, 3 H), 7.56 (d, *J* = 7.2 Hz, 2 H), 7.66 (d, *J* = 7.7 Hz, 2 H), 7.88 (d, *J* = 7.7 Hz, 2 H), 10.0 (s, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ = 126.9, 127.3, 128.5, 128.9, 130.3, 132.2, 135.3, 136.5, 143.4, 191.7.

1-{4-[(*E*)-2-Phenylvinyl]phenyl}ethanone (3t)

Pale-yellow solid; yield: 142 mg (64%); mp 143–145 °C (Lit.²² 144–145 °C). ¹H NMR (300 MHz, CDCl₃): δ = 2.62 (s, 3 H), 7.13 (d, *J* = 16.3 Hz, 1 H), 7.24 (d, *J* = 16.3 Hz, 1 H), 7.28–7.33 (m, 1 H), 7.39 (t, *J* = 7.2 Hz, 2 H), 7.54 (d, *J* = 7.8 Hz, 2 H), 7.59 (d, *J* = 8.2 Hz, 2 H), 7.96 (d, *J* = 8.2 Hz, 2 H). ¹³C NMR (75 MHz, CDCl₃): δ = 26.6, 126.5, 126.8, 127.4, 128.3, 128.8, 128.9, 131.5, 135.9, 136.7, 142.0, 197.5.

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