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Note

Cyclopalladated ferrocenylimines: highly active catalysts for Heck reactions

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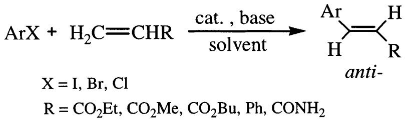
Abstract

A novel kind of ferrocene moiety containing palladacycle catalysts **1** and **2** was synthesized and applied to Heck arylation. High yields, turnover numbers and regioselectivity were achieved in moderate conditions. When 2.73×10^{-8} mol catalyst **2** was used to catalyze arylation of 0.1 mol iodobenzene with butyl acrylate, optimal results were obtained with 3.6×10^6 turnover number and 99% yield. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cyclometallation; Ferrocenylimine; Heck reaction

As one of the most important C–C formation reactions and the only known one-step method for the arylation of olefins, Heck reaction has attracted much research interest [1a–f]. Generally, two kinds of catalysts were employed. One was the coordination complexes of palladium salts such as $Pd(OAc)_2$ or $PdCl_2$ with ligands PPh_3 or PR_3 [2a–d]; the other was cyclopalladium phosphine catalysts [3a–d]. The use of nitrogen-containing catalysts is still rare [4a,b]. This paper reports phosphine-free cyclopalladated ferrocenylimines **1** and **2** as a new kind of catalysts used in Heck reactions for arylation of olefin derivatives with iodobenzene or other arylhalides.



The dimeric complexes **1** and **2** in which the metal center is stabilized by a five-membered ring are readily prepared by treatment of ferrocenylimines with Li_2PdCl_4 or K_2PdI_2 in methanol [5a,b].

Acrylates, styrene, and acrylamide were employed as substrates. All the reactions were accomplished in air at 100 (1,4-dioxane as solvent) or 140 °C (DMF as solvent) with high yields and regioselectivity in several or sometimes scores or hundreds of hours. The configurations of the products were characterized by ^{1}H-NMR spectroscopy. The results are listed in Table 1.

It can be seen from Table 1 that triethylamine used as base is much superior to Na_2CO_3 in this reaction (entries 1 and 12 *vs*. entries 2 and 13, respectively). By comparing entry 2 with entry 3 and entry 4 with entry 5, it was found that reducing the amount of catalysts resulted in a small decrease in yields but a significant increase in turnover numbers. This implied the possibility to acquire high turnover number and turnover number frequency by reducing the percentage of the catalysts. When 2.73×10^{-8} mol of catalyst **2** was used to catalyze the olefination of iodobenzene with ethyl acrylate, 1 379 100 turnover number and 24 620 turnover number frequencies were obtained (entry 6). Furthermore, using 2.73×10^{-8} mol of catalyst **2** to catalyze olefination of iodobenzene with butyl acrylate, the high turnover number of 3.6 million was obtained (entry 10).

From entries 12–15, it can been seen that catalyst **2** showed a higher efficiency in the coupling of iodoben-

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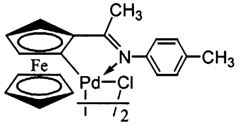
Table 1
Results of the Heck reactions with catalysts **1** and **2**[abcdef]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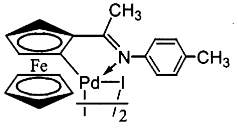
2

Entry	ArX	Amt of ArX [a] (mmol)	R	Catalyst (mmol) $\times 10^{-5}$	Base	T [b] (°C)	Time (h)	Yield [c] (%)	TON	TOF [d]
1	PhI	10	CO_2Et	**1** (100)	Na_2CO_3	100	60	3.12	310	5
2	PhI	10	CO_2Et	**1** (327)	Et_3N	100	2.5	98.7	3020	1200
3	PhI	10	CO_2Et	**1** (3.27)	Et_3N	100	10	91.3	279 200	27 920
4	PhI	10	CO_2Et	**2** (273)	Et_3N	100	2.5	95.4	3500	1400
5	PhI	10	CO_2Et	**2** (2.7)	Et_3N	100	10	86.3	319 600	31 960
6	PhI	50	CO_2Et	**2** (2.73)	Et_3N	100	56	75.3	1 379 100	24 620
7	PhI	10	CO_2Me	**2** (91)	Et_3N	100	3	99.9	10 980	3660
8	PhI	10	CO_2Bu	**1** (109)	Et_3N	100	3	99.9	9160	3050
9	PhI	10	CO_2Bu	**2** (91)	Et_3N	100	3	98.5	10 800	3600
10	PhI	100	CO_2Bu	**2** (2.73)	Et_3N	100	145	99.0	3 626 000	25 000
11	PhI	80	CO_2Bu	**2** (1)	Et_3N	100	338	92 [e]	7 360 000	21 700
12	PhI	10	Ph	**1** (100)	Na_2CO_3	100	60	2.9	290	4
13	PhI	10	Ph	**1** (327)	Et_3N	100	8	38.2	1160	140
14	PhI	10	Ph	**2** (273)	Et_3N	100	8	99.3	3630	450
15	PhI	10	Ph	**2** (2.73)	Et_3N	100	70	71.2	260 800	3720
16	PhI	12	$CONH_2$	**2** (91)	Et_3N	100	9	66.8	8800	970
17	PhI	10	$CONH_2$	**2** (91)	Et_3N	100	15	88.7	9750	650
18	p-NO_2PhBr [f]	10	CO_2Et	**2** (1820)	Et_3N	100	10	100	550	50
19	p-NO_2PhBr [f]	10	CO_2Et	**2** (273)	Et_3N	140	4	100	3660	910
20	p-NO_2PhBr [f]	100	CO_2Et	**2** (2.73)	Et_3N	140	55	64	2 340 000	42 500
21	p-NO_2PhCl [f]	10	CO_2Et	**2** (1820)	Et_3N	140	10	73	400	40

[a] Mol ratios PhI / olefin / Et_3N = 1:1.5:1, PhI / olefin / Na_2CO_3 = 1:1.5:0.5 except entry 11, 18-21.

[b] The reactions at 100°C and 140°C were conducted in 1,4-dioxane and DMF respectivily.

[c] All the yields were isolated yields based on ArX except entry 11.

[d] TON = (moles of ArX) × (%yield) / (moles of catalyst added), TOF = TON / (hours of reaction), TON and TOF were not optimized.

[e] Mol ratio PhI / olefine / base = 1:1.2:1.2. Yield determined by HPLC, based on iodobenzene and the product (trans $PhCH=CHCO_2R$).

[f] Mol ratios ArX /olefine / base/ Bu_4NBr = 1:1.5:1:1.

zene with styrene than catalyst **1**, probably due to catalyst **2** being more soluble than catalyst **1**. The coupling reactions of iodobenzene with acrylamide gave moderate to good yields of *trans*-cinnamamide.

It is noteworthy that all of these reactions studied showed high regioseletivity for *trans*-coupling, and no *cis*-product was found.

Besides, the figure of 7.36 million turnovers was obtained by reducing the amount of catalyst **2** to 1×10^{-8} mol and prolonging the reaction time to 338 h in the case of arylation of iodobenzene with butyl acrylate. The experiment indicated that there were no changes in the catalytic activity during the repeated uses of catalyst **2** in the arylation of iodobenzene with ethyl acrylate for five times. In the case of arylation of bromobenzene or substituted bromobenzene with ethyl acrylate by using catalyst **2**, moderate to 100% yields and hundreds to 2.34 million turnovers (in the case of p-NO_2PhBr used as substrate) were obtained. By using catalyst **2**, arylation of p-NO_2PhCl with ethyl acrylate in DMF, 140 °C for 10 h, 73% yield (TON 400) was obtained.

In summary, the cyclopalladated ferrocenylimines showed exceedingly high catalytic activities and yields in olefination of iodobenzene, unactivated aryl bromides or chlorides. The high activities in the olefination of iodobenzene were observed in mild reaction conditions without any additive. Further study on the reaction mechanism is in progress.

1. Experimental

1.1. General procedure for Heck reaction of iodobenzene

Ten millimoles of iodobenzene, 15 mmol of olefin, 10 mmol of Et_3N (or 5 mmol Na_2CO_3) and catalyst were dissolved in 3 ml 1,4-dioxane and stirred at about 100 °C in an oil bath. After cooling, the reaction mixture was diluted with water and extracted with CH_2Cl_2 for four times. The combined organic phase was dried with Na_2SO_4. After removal of the solvent *in vacuo*, the product was isolated by thin layer chromatography (except entry 11).

1.2. Synthesis of cyclopalladated ferrocenylimines

Ferrocenylimine was prepared according to the published procedure [5a]. Ferrocenylimine and mole equivalent NaOAc were added to the MeOH solution of mole equivalent Li_2PdCl_4 or K_2PdI_4, the resulting red solutions were stirred at room temperature for about 20 h and then filtered, the solid cyclopalladated ferrocenylimines obtained were washed with MeOH.

Catalyst **1** $[\{[Pd(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3)C(CH_3){=}N(C_6H_4CH_3\text{-}4)](\mu\text{-}Cl)\}_2]$ was a red crystal, yield 92.4%, m.p. (dec.) > 210 °C. IR (cm^{-1}): 3090, 2920, 1551, 1508, 1474, 1105, 999, 817, 721, 693. ^1H-NMR (DMSO-d_6): 2.01 (s, 6H, CH_3), 2.31 (s, 6H, CH_3), 4.38 (s, 10H, C_5H_5), 4.48 (bs, 2H, H-4), 4.73 (bs, 2H, H-5), 5.14 (bs, 2H, H-3), 6.94 (d, $J = 6.8$ Hz, 4H, C_6H_4), 7.14 (d, $J = 8$ Hz, 4H, C_6H_4). Anal. Found: C, 49.92; H, 3.91; N, 2.93. Calc. for $C_{38}H_{36}N_2Cl_2Fe_2Pd_2$: C, 49.82; H, 3.96; N, 3.06%.

Catalyst **2** $[\{[Pd(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3)C(CH_3){=}N(C_6H_4CH_3\text{-}4)](\mu\text{-}I)\}_2]$ was an orange red crystal, yield 86.9%, m.p. (dec.) > 230 °C. IR (cm^{-1}): 3088, 2918, 1562, 1508, 1474, 1106, 1000, 817, 722, 663. ^1H-NMR (DMSO-d_6): 2.01 (s, 6H, CH_3), 2.32 (s, 6H, CH_3), 4.34 (s, 10H, C_5H_5), 4.37 (bs, 2H, H-4), 4.62 (bs, 2H, H-5), 5.02 (bs, 2H, H-3), 6.94 (d, $J = 8$ Hz, 4H, C_6H_4), 7.22 (d, $J = 8$ Hz, 4H, C_6H_4). Anal. Found: C, 41.59; H, 3.43; N, 2.62. Calc. for $C_{38}H_{36}N_2I_2Fe_2Pd_2$: C, 41.53; H, 3.30; N, 2.55%.

Acknowledgements

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