Pergamon

Tetrahedron Letters 42 (2001) 7877–7878

TETRAHEDRON
LETTERS

Acetylferrocenyloxime palladacycle-catalyzed Heck reactions[†]

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Received 16 July 2001; revised 13 August 2001; accepted 24 August 2001

Abstract—Acetylferrocenyloxime palladacycle catalyzed the Heck reaction of aryl bromides and activated aryl chlorides. © 2001 Elsevier Science Ltd. All rights reserved.

Several novel palladacycles have been reported in recent times to catalyze the Heck reaction of aryl halides with olefins, the advantages being the longer life time of the catalysts and more efficient catalysis. Cyclopalladated aromatic rings are the choice systems for such catalysts as the starting materials offer a wide variety of substituents and are readily available and easily cyclopalladated. A variety of palladacycles incorporating cyclometallated phosphine,[1] phosphite,[2] carbene,[3] imine,[4] thioether[5] and oxime[6] have been reported with high turnover numbers upto 10^5–10^6.

These palladacycles are both thermally and oxidatively stable and the catalytic cycle operates through Pd(II)–Pd(IV) instead of the traditional Pd(0)–Pd(II) mechanism.

Cyclopalladation of substituted ferrocenes is facile and these complexes could be excellent catalysts for the Heck reaction. Acetylferrocenyl oxime was cyclopalladated according to the reported literature procedure to give the dimeric acetylferrocenyl oxime palladacycle **1**, which was then converted into the monomeric complexes **2** and **3** by treatment with PPh_3 and $P(OEt)_3$[7] (Scheme 1). These complexes are thermally stable and are also not sensitive to oxygen and moisture because of the stable five-membered ring palladacycle.

The Heck reaction between 4-iodoanisole and ethyl acrylate or styrene proceeded readily in NMP as solvent and catalyzed by complex **1** under standard conditions (catalyst 0.01 mmol, ArX 2 mmol, olefin 2–5 mmol, NaOAc 4 mmol, NMP 5 mL, reaction tempera-

Table 1. Acetylferrocenyloxime palladacycle catalyzed Heck reactions

Serial no.	Aryl halide (ArX)	Olefin	Yield (%)		
			Cat **1**[a]	Cat **2**[a]	Cat **3**[a]
1	4-Iodoanisole	Ethyl acrylate	74	93	93
2	4-Iodoanisole	Styrene	69	67	73
3	Bromobenzene	Ethyl acrylate	47	58	70
4	Bromobenzene	Styrene	55	60	72
5	4-Bromophenol	Ethyl acrylate	24	20	45
6	1-Bromonaphthalene	Ethyl acrylate	76	66	61
7	1-Bromonaphthalene	Styrene	81	81	79
8	4-Chloroacetophenone	Styrene	30	53	18

[a] Catalyst **1**, **2** or **3**. See Scheme 1.
Reaction conditions: Catalyst concentration, 0.01 mmol; ArX, 2 mmol; olefin, 2–5 mmol; base, NaOAc (2 equiv.); temperature, 140–150°C; solvent, NMP.

Keywords: acetylferrocenyloxime palladacycle; Heck reaction; aryl bromides.

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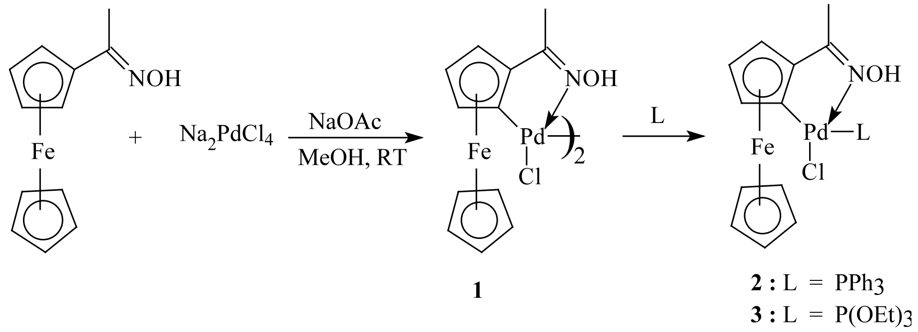
[†] NCL Communication No. 6610.

PII: S0040-4039(01)01604-5



Scheme 1.

Table 2. Acetylferrocenyloxime palladacycle catalyzed Heck reaction at low catalyst concentrations

Serial no.	Aryl halide (ArX)	Olefin	Yield (%)		
			Cat **1**[a] (TON)	Cat **2**[a] (TON)	Cat **3**[a] (TON)
1	4-Iodoanisole	Ethyl acrylate	65 (62500)	84 (14000)	92 (15333)
2	4-Iodoanisole	Styrene	73	67	69
3	Bromobenzene	Ethyl acrylate	79 (15192)	78 (13000)	77 (10694)
4	Bromobenzene	Styrene	84 (7000)	79 (5266)	83 (5533)
5	4-Bromophenol	Ethyl acrylate	45	20	24
6	1-Bromonaphthalene	Ethyl acrylate	83 (31923)	86 (28666)	90 (25000)
7	1-Bromonaphthalene	Styrene	94 (36153)	91 (30333)	97 (26944)
8	4-Chloroacetophenone	Styrene	30 (38)[b]	–	53 (81)[b]
9	4-Chlorobenzonitrile	Styrene	22 (28)[b]	–	37 (58)[b]

[a] Catalyst **1**, **2** or **3**. Scheme 1.

[b] Bu_4NBr, 1 mmol.

Reaction conditions: Catalyst concentration, 2.6×10^{-4} mmol to 1.3×10^{-3} mmol; ArX, 10–25 mmol; olefin, 10–50 mmol; base, NaOAc (2 equiv.); temperature, 140–150°C; solvent, NMP.

ture 140–150°C) to give ethyl (*E*)-4-methoxycinnamate and (*E*)-4-methoxystilbene in 74 and 69% yields, respectively. The monomeric catalysts **2** and **3** gave a 93% yield of ethyl (*E*)-4-methoxycinnamate and 73 and 67% yields of (*E*)-4-methoxystilbene (Table 1). The reaction of 25 mmol of 4-iodoanisole with ethyl acrylate (50 mmol) in the presence of 2.6×10^{-4} mmol of catalyst **1** gave the ethyl (*E*)-4-methoxycinnamate in 65% yield with a turnover number of 62500. Increasing the catalyst concentration to 1.3×10^{-3} led to a shorter reaction time, but did not improve the yield (76–84%). The catalysts **2** and **3** gave 84 and 92% yields of ethyl (*E*)-4-methoxycinnamate (catalyst concentration 1.5×10^{-3} mmol) (Table 2).

Complexes **1**, **2** and **3** 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 (TONs 5266–15192). 1-Bromonaphthalene showed excellent reactivity with both ethyl acrylate and styrene to give ethyl (*E*)-3-(1-naphthyl) propenoate and (*E*)-2-phenyl-1-(1-naphthyl) ethene in 83–97% yield (TONs 25000–36153). NaOAc was a better base than K_2CO_3. 4-Bromophenol reacted with ethyl acrylate to give the ethyl-4-(*E*)-hydroxycinnamate in only 20–45% yields.

Activated aryl chlorides, such as 4-chloroacetophenone and 4-chlorobenzonitrile, also reacted with styrene to give the corresponding stilbenes in moderate yields (22–53%). The phosphite complex **3** gave the highest yields of the substituted products. The acetylferrocenyloxime palladacycles are thus excellent catalysts for the Heck reaction, though not as active as the previously reported acetophenone and benzophenone oxime palladacycles.[5]

Acknowledgements

We thank the DST for research funds and CSIR for a JRF to A.J.

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