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Note

Cyclopalladated complexes of tertiary arylamines as highly efficient catalysts using in the Heck reactions

Fan Yang, Yangming Zhang, Rui Zheng, Jie Tang *, Mingyuan He

Center for the Chemistry of Ionic Liquids, Department of Chemistry, East China Normal University, 3663 Zhongshanbei Road, Shanghai 200062, China

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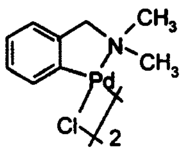
Abstract

Cyclopalladated complexes of tertiary arylamines are reported in this paper as highly efficient catalysts for the Heck reactions of iodoarenes with methylacrylate. The monomeric complexes (**2** and **4**), which contain mixed phosphorous–nitrogen (P–N) donors, were found to be more active than the corresponding dimeric ones, which contain only single nitrogen donor. Palladium mirror was observed, indicating the involvement of classic Pd(0)/Pd(II) catalytic cycle using these cyclopalladated complexes.

Keywords: Heck reaction; Cyclopalladated complex; Palladium mirror; Palladium catalyst

Olefination of aryl halides, known as the Heck reactions, is an important transition-metal-catalyzed reaction for organic synthesis [1]. However, these coupling reactions used to suffer from the need of high amounts of palladium catalyst (1–5 mol%). Recently, very efficient catalysis using cyclopalladated phosphines [2], phosphites [3] and imines [4], carbene [5], and dimethylglycine [6] have been investigated, but the Heck reactions catalyzed by cyclopalladated tertiary arylamines have rarely been reported. This paper reports a study on the catalytic activity of these complexes using in the Heck reactions of iodoarenes with methyl acrylate with turnover numbers (TON) more than 10^6 in some cases. Among complexes **1**–**4**, the monomeric complexes (**2** and **4**), which contain mixed phosphorous–nitrogen (P–N) donors, were found to be more active than the corresponding dimeric ones (**1** and **3**), which contain only single nitrogen donor. In the coupling of iodobenzene with methylacrylate catalyzed by complex **4** in DMA (*N*,*N*-dimethylacetamide) at 140 °C, the TON up to 9 600 000 and turnover frequencies (TOF) up to 870 000 were obtained, respectively. This is the highest catalytic activity of all Heck reactions reported to date.



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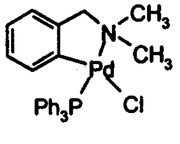

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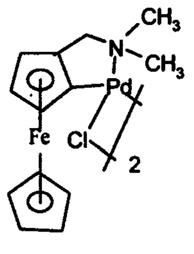

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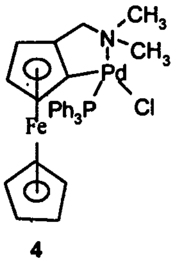

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The complexes **1**–**4** are thermally stable and not sensitive to oxygen and moisture for the metal center are stabilized by a five-member ring. These complexes were conveniently prepared according to the literature methods [7]. For example, the dimeric complexes are readily prepared by treatment of $Li_2[PdCl_4]$ or

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* Corresponding author. Fax: 86-21-5251-0411.
E-mail address: tangecnu@sina.com (J. Tang).

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Table 1
Heck reactions of iodobenzene with methylacrylate [a]

Run	Solvent	Catalyst	Yield (%) [b]
1	1,4-Dioxane	**1**	34
2	1,4-Dioxane	**2**	55
3	Toluene	**1**	35
4	Toluene	**2**	58
5	Mesitylene	**1**	38
6	Mesitylene	**2**	66
7	DMA [c]	**1**	81
8	DMA	**2**	100

[a] All reactions were carried out with 5 mmol of PhI, 6 mmol of methylacrylate, 7 mmol of NEt_3 and 0.1 mol% catalyst in 10 ml of solvent for 1.5 h at 140 °C.

[b] Determined by GC, based on iodobenzene.

[c] *N*,*N*-Dimethylacetamide.

$Na_2[PdCl_4]$ with the corresponding amines, and the monomeric complexes are obtained immediately by treatment of PPh_3 with the respective dimers in benzene.

In order to find a suitable solvent, the Heck reactions of iodobenzene with methylacrylate catalyzed by complexes **1** or **2** were examined with a number of solvents. The results are summarized in Table 1. The reaction can be carried out in low polar solvents (1,4-dioxane) or non-polar solvents (mesitylene), although at relatively low rates. Of all solvents tested, DMA was found to be the best one. So the after reactions were all carried out in DMA and the results are summarized in Table 2.

The results in Table 2 showed that complexes **1**–**4** are more efficient for the Heck reactions with TON of 10^6 in some cases as compared with traditional catalysts $Pd(PPh_3)_4$ or PdX_2–PPh_3. Meanwhile, the monomeric complexes (**2** and **4**) were more active than the corresponding dimeric ones (**1** and **3**) (runs 1–8 in Table 1 and runs 5–8 in Table 2). In the coupling of iodobenzene with methylacrylate catalyzed by 1×10^{-5} mol% of complex **4**, the highest TON of 9 600 000 and TOF of 870 000 of all Heck reactions reported to date were obtained (run 8 in Table 2). The best TON reported previously for Heck reactions was 8 900 000 in the coupling of iodobenzene with *n*-butyl acrylate under a higher temperature (180 °C) [3]. In addition, complex **2**, whose structure is similar to complex **4**, also showed outstanding catalytic activity with the TON of 9 100 000 and TOF of 830 000 (run 6, Table 2). This is also among the highest catalytic activity for Heck reactions. In view of the simplicity and efficiency, complexes **2** and **4** are very attractive for industrial application.

Complexes **2** and **4** also exhibited fairly high activities when the iodoarenes with electron donating groups were used as the substrates. In the cases of reactions of *p*-iodotoluene and *p*-iodophenol with methylacrylate, catalyzed by 0.01 mol% of complexes **2** and **4**, the Heck products were obtained in good yields (runs 9–12 in Table 2). For these deactivated iodoarenes, the yields of Heck products depended much on the amounts of catalysts used. For example, when 0.001 mmol% of complex **4** was used, the Heck products were obtained only in 89 and 45% yield for *p*-iodotoluene and *p*-

Table 2
Results of Heck reactions of iodoarenes in DMA [a]

Run	ArX	Catalyst (mol%Pd)	*t* (h)	*T* (°C)	Yield (%) [b]	TON/TOF
1	PhI	**1** (1×10^{-3})	11	140	99	99 000/9000
2	PhI	**2** (1×10^{-3})	11	140	100	100 000/9100
3	PhI	**3** (1×10^{-3})	11	140	99	99 000/9000
4	PhI	**4** (1×10^{-3})	11	140	100	100 000/9100
5	PhI	**1** (1×10^{-5})	11	140	34	3 400 000/310 000
6	PhI	**2** (1×10^{-5})	11	140	91	9 100 000/830 000
7	PhI	**3** (1×10^{-5})	11	140	33	3 000 000/300 000
8	PhI	**4** (1×10^{-5})	11	140	96	9 600 000/870 000
9	*p*-MePhI	**2** (1×10^{-2})	11	140	97	9700/880
10	*p*-MePhI	**4** (1×10^{-2})	11	140	99	9900/900
11	*p*-HOPhI	**2** (1×10^{-2})	11	140	93	9300/850
12	*p*-HOPhI	**4** (1×10^{-2})	11	140	94	9400/850
13	*p*-MePhI	**4** (1×10^{-3})	11	140	89	89 000/8100
14	*p*-HOPhI	**4** (1×10^{-3})	11	140	45	45 000/4100
15	*p*-MePhI	**4** (1×10^{-3})	22	160	94	94 000/4300
16	*p*-HOPhI	**4** (1×10^{-3})	22	160	46	46 000/2100
17	PhBr	**1** (1×10^{-3})	11	140	<1	_
18	PhBr	**2** (1×10^{-3})	11	140	<1	_
19	PhBr	**3** (1×10^{-3})	11	140	<1	_
20	PhBr	**4** (1×10^{-3})	11	140	<1	_

[a] All reactions were carried out with 5 mmol of ArI–PhBr, 6 mmol of methylacrylate and 7 mmol of NEt_3 in 10 ml of DMA.

[b] Determined by GC, based on iodoarenes.

iodophenol, respectively (runs 13 and 14, Table 2). Longer reaction time and higher reaction temperature turned out to be little improvement (runs 15 and 16, Table 2). Moreover, the reaction of bromobenzene was carries out under the same conditions (runs 17–20 in Table 2), and the results indicate that only traces of products were yielded.

The issue of a possible Pd(II)/Pd(IV) cycle in Heck catalysis is currently under debate, particularly for cyclopalladated complexes [9]. In our cases, we think the major pathway of the reactions is via a Pd(0)/Pd(II) cycle, since similar catalytic activity was observed for different catalysts (runs 5 and 7, runs 6 and 8, Table 2). Moreover, when 0.1 mmol% of complex **4** was used in the coupling reaction of iodobenzene with methylacrylate at the same conditions except under a lower temperature (80 °C), a beautiful palladium mirror was observed on the wall of the flask at the end of reaction. The observed palladium mirror assured the formation of Pd(0) species during the reaction. As far as we know, there is no report on palladium mirror formation in Heck reactions catalyzed by cyclopalladated complexes. The possible Pd(II)/Pd(IV) cycle cannot be ruled out in our cases either; it may function as a side pathway.

However, what interests us now is the remarkable difference in the catalytic activity shown by the monomeric complexes and the dimeric ones. We suppose that the catalytic difference resulted from the triphenylphosphine part, which is the main difference in their structures. In many Heck reactions, tertiary phosphine, usually triphenylphosphine, is required to furnish the reaction [5]. It is also widely accepted that $Pd(OAc)_2$ employed in the catalytic systems, generally in combination with tertiary phosphine ligands, is reduced to the catalytically active palladium(0) species in the presence of base, such as, triethyl amine [8]. We assumed that the monomeric complexes **2** and **4** are easier to be reduced to the active Pd(0) species compared with the corresponding dimeric ones under the same conditions. The in situ generated Pd(0) species probably were the actually active catalysts, thus resulted in the different catalytic activity observed in our investigation.

In summary, we have found that cyclopalladated complexes of tertiary arylamines **1**–**4** are active catalysts for Heck reactions of iodoarenes with methylacrylate in contrast with traditional palladium catalysts. Meanwhile, the monomeric complexes (**2** and **4**) were found to be more efficient than the corresponding dimeric ones (**1** and **3**). The palladium mirror observed at the end of the reaction is a support for the classic Pd(0)/Pd(II) cycle. Further studies on the palladium mirror formation and the application of these complexes for other substrates are currently in progress.

1. Experimental

All GC results were recorded on a SRI8610C chromatograph.

1.1. General procedure

In a 25 ml flask were placed 5 mmol of ArI, 6 mmol of methylacrylate, 7 mmol of NEt_3, 0.1 mol% catalyst and 10 ml of solvent. The reaction mixture was stirred at 140 °C for a period of time, and determined by GC based on iodobenzene. The product was identified by comparison with authentic sample.

Acknowledgements

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