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1,3-Dicarbonyl compounds as phosphine-free ligands for Pd-catalyzed Heck and Suzuki reactions

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Abstract

Some 1,3-dicarbonyl compounds (such as pentane-2,4-dione and 3-oxo-*N*-phenylbutanamide) were found to constitute highly efficient, yet low-priced and phosphine-free ligands for the Pd-catalyzed Heck and Suzuki reactions of aryl bromides and iodides with very high turnover numbers (ca. 10^3–10^4).

Keywords: Palladium catalyst; Suzuki reaction; Heck reaction; Phosphine-free ligand

Pd-catalyzed coupling reactions have been widely used in the synthesis of various organic compounds ranging from natural products to photo-electronic materials [1]. These reactions, normally performed with 1–5 mol% of Pd catalyst along with equal or higher mole amounts of phosphine ligands, still suffer from two significant problems [2]. First, Pd is expensive, and contamination of the product by Pd often has to be tightly controlled. Second, many phosphine ligands are even more expensive than Pd, and they are not pleasant to work with, because they are poisonous, air sensitive, and prone to degrade.

A solution to the above two problems is to develop high turnover-number catalysts (TON > 10^3) that utilize non-phosphine ligands. In this regard, a number of phosphine-free catalysts were recently reported for Pd-catalyzed Heck and Suzuki reactions. In these catalysts the ligands are either heterocyclic carbenes or nitrogen-containing compounds and heterocycles, where the coordinating atoms are carbon or nitrogen [3]. Here we report our new finding that 1,3-dicarbonyl compounds can also be used as phosphine-free ligands for Pd-catalyzed Heck and Suzuki reactions where the coordinating atom is oxygen. Noteworthily 1,3-dicarbonyl compounds were discovered in 2002 by Song and co-workers to be useful ligands for Cu-catalyzed Ullmann diaryl ether synthesis [4]. More recently Buchwald and Shafir discovered that a 1,3-dicarbonyl ligand could facilitate Cu-catalyzed C–N coupling reactions [5]. Despite these interesting reports, very little has been known about the effects of 1,3-dicarbonyl ligands in Pd-catalyzed transformations.

To begin our study, we examined the Heck reaction between bromobenzene and styrene (Table 1). Previously we found that without any ligand the yield of this reaction was as low as 15% after 10 h at 0.1 mol% loading of Pd [6]. Addition of ligand **L1** dramatically increased the yield to 99% in 2 h at 0.1 mol% Pd loading (entry 1) (Table 1). Further decrease of Pd loading to 0.01 mol%, however, resulted in a much poorer catalyst performance (entry 2). Inspired by this finding, we synthesized a variety of 1,3-dicarbonyl compounds and examined their effects in the Heck

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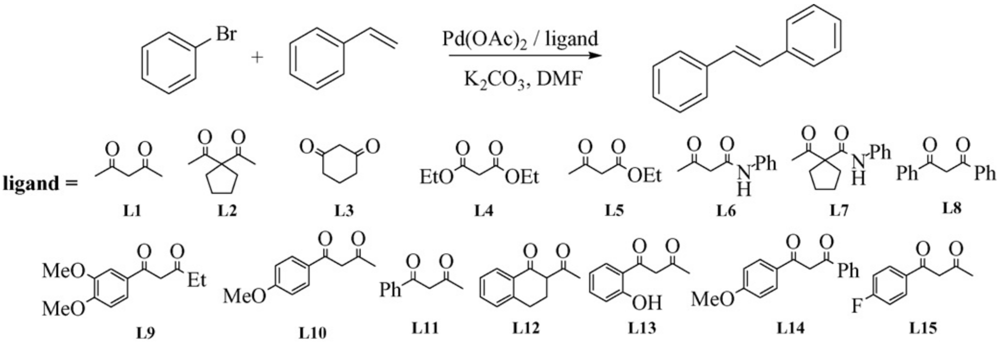
Table 1
Heck reaction between bromobenzene and styrene[a]

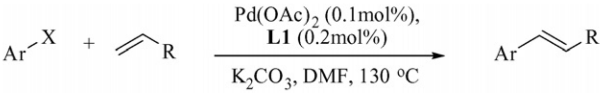


Entry	Ligand	Pd loading (mol%)	Time (h)	Yield (%)[b]	Entry	Ligand	Pd loading (mol%)	Time (h)	Yield (%)[b]
1	**L1**	0.1	2	99	9	**L8**	0.1	10	43
2	**L1**	0.01	10	81	10	**L9**	0.1	2	2
3	**L2**	0.1	2	6	11	**L10**	0.1	2	78
4	**L3**	0.1	4	71	12	**L11**	0.1	10	71
5	**L4**	0.1	2	53	13	**L12**	0.1	2	36
6	**L5**	0.1	4	49	14	**L13**	0.1	4	17
7	**L6**	0.1	2	99	15	**L14**	0.1	4	29
8	**L7**	0.1	2	8	16	**L15**	0.1	2	62

[a] Reaction conditions: bromobenzene (0.5 mmol), styrene (0.75 mmol), K_2CO_3 (1 mmol), Pd/ligand = 1:2, DMF (1 mL), 130 °C, under Ar.
[b] GC yields.

reaction [7]. It was found that ligand **L2**, **L7**, and **L9** produced negative, if not zero, effects on the Heck reaction. On the other hand, ligand **L3**, **L6**, **L10**, and **L11** significantly improved the Heck reaction as compared to the ligand-free conditions. Nonetheless, only **L1**and **L6** could provide a nearly quantitative yield in 2 h. Therefore, these two ligands constituted practically interesting phosphine-free ligands for Pd-catalyzed transformations.

Table 2
Heck reactions between aryl halides and olefins facilitated by ligand **L1**[a]



Entry	ArX	R	Time (h)	Yield[b] (%)	Entry	ArX	R	Time (h)	Yield[b] (%)
1	PhBr	Ph	2	99	16	4-NC-C_6H_4Br	Ph	2	98
2	PhBr	CO_2Bu^n	2	99	17	4-NC-C_6H_4Br	CO_2Bu^n	2	93
3	4-O_2N-C_6H_4Br	Ph	2	96	18	4-Ph-C_6H_4Br	Ph	2	84
4	4-O_2N-C_6H_4Br	CO_2Bu^n	2	98	19	4-Ph-C_6H_4Br	CO_2Bu^n	2	89
5	4-Me-C_6H_4Br	Ph	2	96	20	3-F_3C-C_6H_4Br	Ph	2	99
6	4-Me-C_6H_4Br	CO_2Bu^n	2	97	21	3-F_3C-C_6H_4Br	CO_2Bu^n	2	99
7	1-$C_{10}H_7Br$	CO_2Bu^n	2	94	22	3-Bromopyridine	Ph	2	98
8	4-MeO-C_6H_4Br	Ph	4	97	23	3-Bromopyridine	CO_2Bu^n	2	98
9	4-MeO-C_6H_4Br	CO_2Bu^n	4	99	24	PhI	Ph	10	99
10	4-OHC-C_6H_4Br	Ph	2	99	25	PhI	CO_2Bu^n	10	99
11	4-OHC-C_6H_4Br	CO_2Bu^n	2	98	26	4-MeO-C_6H_4I	Ph	10	98
12	4-MeOC-C_6H_4Br	Ph	2	97	27	4-MeO-C_6H_4I	CO_2Bu^n	10	99
13	4-MeOC-C_6H_4Br	CO_2Bu^n	2	99	28	4-MeOC-C_6H_4I	Ph	10	96
14	3-NC-C_6H_4Br	Ph	2	99	29	4-MeOC-C_6H_4I	CO_2Bu^n	10	98
15	3-NC-C_6H_4Br	CO_2Bu^n	2	95	30	4-O_2N-C_6H_4Cl	Ph	20	10

[a] Reaction conditions: bromobenzene (0.5 mmol), olefin (0.75 mmol), K_2CO_3 (1 mmol), DMF (1 mL), under Ar.
[b] Isolated yield.