Photochemical C-C Bond Formation from Chlorobenzene Mediated by [Pd(PPh$_3$)$_4$]

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Photo-irradiation upon the chlorobenzene solution of [Pd(PPh$_3$)$_4$] affords *trans*-[PdCl$_2$(PPh$_3$)$_2$] and a mixture of chlorobiphenyls. In the presence of zinc and organic amines, the catalytic production of chlorobiphenyls mediated by the palladium complex was observed with irradiation of light.

Photochemistry of low-valent d^{10} metal complexes has received a special attention in recent years.[1] The excited states of the complexes often have long lifetime even in fluid solution to lead to interesting chemical reactions. A lot of systems showing photoredox reactions have been reported.[2]

Caspar reported the photochemistry and photophysics of [Pd(PPh$_3$)$_4$] (**1**) in 1985. He showed that the irradiation of near UV light upon the chlorobenzene solution of **1** gives *trans*-[PdCl(C$_6$H$_5$)(PPh$_3$)$_2$] (**2**).[3] We found further irradiation causes a subsequent photochemical reaction. Figure 1 shows the changes in the absorption spectra of the solution of **1** with irradiation of light (a high-pressure mercury lamp equipped with a glass filter, $\lambda > 350$ nm). Since **1** was reported to dissociate into [Pd(PPh$_3$)$_3$] in benzene,[4] the Pd^0 complex having a 320 nm band must be the tris complex. At first, the intensity of the absorption band at 320 nm decreased rapidly, and then a new band grew more slowly at 350 nm. The initial reaction corresponds to the oxidative addition of chlorobenzene to the palladium center, which was described by Caspar. Since further dissociation of the phosphine ligand from the Pd(0) complex is reported to be unlikely,[5] the Pd(0) complex in the excited state should be an active species. We obtained a yellow complex after the second reaction, which was identified as *trans*-[PdCl$_2$(PPh$_3$)$_2$] (**3**) by UV absorption and ^{31}P-NMR spectra. The 350 nm band shown in Figure 1 was assigned to **3**. In the second step of the photochemical reaction, the formation of the three isomers of chlorobiphenyl was confirmed by gas chromatography. The observed total yield of the three chlorobiphenyls is 120% based on the starting palladium(0) complex.[6] The isomer ratio of 2- 3- and 4-chlorobiphenyls was determined to be 6 : 2 : 1.

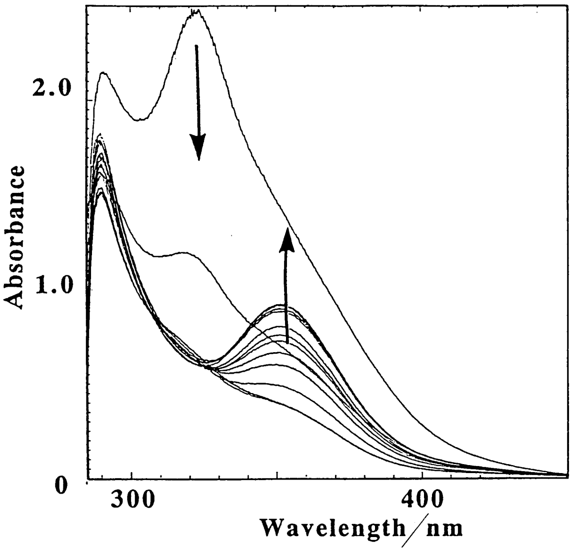


Figure 1 The change in the absorption spectra of [Pd(PPh$_3$)$_4$] in chlorobenzene with irradiation of light.

Coupling reactions of aryl halides using low-valent metal complexes are well-known methods to make biphenyl or bipyridyl derivatives.[7] Both the stoichiometric and catalytic reactions are developed. In order to promote the reactions catalytically, reducing reagents such as zinc have been used.[8] The reducing reagents recover the starting low-valent metal complexes. We studied the photochemical reactions of the palladium complex with chlorobenzene in the presence of zinc powder and organic amines. After the irradiation of light at room temperature, catalytic production of chlorobiphenyls mediated by the palladium(0) complex was observed. The formation of chlorobiphenyls was not observed in the dark.

The results are listed in Table 1. In the experiments, chlorobenzene itself was used as a solvent. The irradiation was performed under argon atmosphere at 20 °C in a thermostatted bath. Other experimental conditions are given in the caption of the table. The isomer ratio of the 2-, 3- and 4-chlorobiphenyls

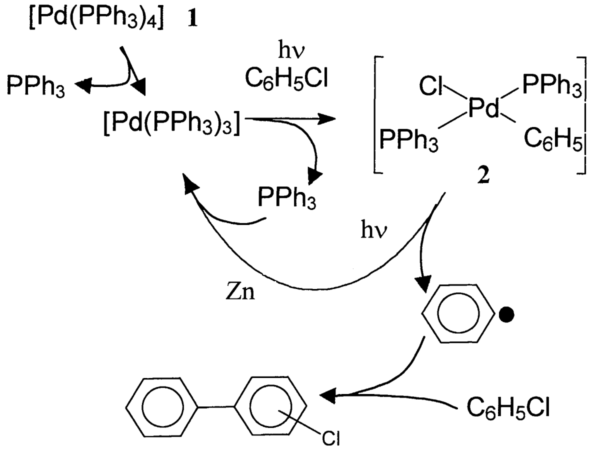
Table 1. Results for the catalytic photoreaction.[a] The amounts of the added zinc, base and the products are shown based on the palladium complex used

run	[Zn]/[Pd]	[base][b]/[Pd]	catalyst[c]	chlorobiphenyls[d]/[Pd]	additives
1	0	0	**1**	1.2	
2	0	15(A)	**1**	2.3	
3	15	0	**1**	2.4	
4	15	15(A)	**1**	16.9	
5	30	30(A)	**1**	21.1	
6	100	100(A)	**1**	27.3	
7	15	15(B)	**1**	17.0	
8	15	15(C)	**1**	0.5	
9	15	15(D)	**1**	8.7	
10	15	15(E)	**1**	21.9	
11	15	15(A)	**3**	0	
12	15	15(A)	**2**	0.6	
13	15	15(A)	**2**	12.3	+2PPh3
14	15	15(A)	**1**	0	+TEMPO

[a] Experimental conditions; [Pd complexes] = 0.3 mM in chlorobenzene, 6 h-irradiation of high-pressure mercury lamp equipped with a UV-35 filter at 20 °C.
[b] (A) triethylamine, (B) piperidine, (C) proton sponge, (D) 2,6-dimethylpiperidine, (E) 1,2,2,6,6-pentamethylpiperidine
[c] [Pd(PPh$_3$)$_4$], *trans*-[PdCl(C$_6$H$_5$)(PPh$_3$)$_2$], *trans*-[PdCl$_2$(PPh$_3$)$_2$].
[d] Total amounts of three chlorobiphenyl-isomers are shown.

is always 6 : 2 : 1 irrespective of the reaction conditions.

Both zinc powder and organic bases are indispensable for the catalytic reactions (see runs 2 and 3). The effect of the base was studied using a series of organic bases. The pKa values are as follows; triethylamine (10.72) , 2,6-dimethylpyridine (6.90), piperidine (11.20), 1,2,2,6,6-pentamethylpiperidine (11.25), proton sponge (1,8-bis(dimethylamino)naphthalene, 12.34). Generally, the use of amines of high basicity gave good results except for the proton sponge (runs 4,7-10). The amines may play an role to neutralize hydrogen chloride which is formally produced with the reaction. The maximum turnover number is up to 27. The phenyl complex **2** has moderate activity especially when PPh_3 is added. The results suggest that the palladium(II) complex is involved in the catalytic cycle. On the other hand, the dichloro complex **3** has no catalytic activity. The regioselectivity is always constant, *i.e.*, 2, -3-, and 4-substituted biphenyls are obtained in 6 : 2 : 1 ratio. The ratio suggests a radical mechanism.[9] To confirm the participation of a radical in the reaction, a radical scavenger, TEMPO, was used in the reaction. We confirmed that the absorption spectrum of the starting Pd(0) complex was not affected by addition of TEMPO. However, the catalytic reaction was completely inhibited (see run 14). The phenyl radical produced by photo-cleavage of complex **2** is proposed to attack the chlorobenzene molecules. In the stoichiometric reaction without zinc, the formation of the dichloro complex **3** was readily detected from the characteristic absorption band seen at 350 nm. However, in the presence of zinc, the intensity of the absorption around the 350 nm region never increases throughout the photochemical reaction. We propose a reaction scheme for the photochemical reactions in the presence of zinc (Scheme 1). Further mechanistic research should be necessary to clarify the role of the palladium complex and the full picture of the photochemical reactions. It should be noted that the light used in this study (λ > 350nm) cannot be absorbed by the organic substrates itself, and that a key factor of this new photochemical reaction systems should be in the photochemical properties of the palladium complexes.



Scheme 1. Proposed scheme for the Pd-mediated photochemical catalytic reaction of chlorobenzene.

References and Notes

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