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Alkoxycarbonylation of aryl iodides catalyzed by Pd with a thiourea type ligand under balloon pressure of CO

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ABSTRACT

Palladium-catalyzed alkoxycarbonylation of aryl iodides with a thiourea-oxazoline type ligand has been achieved under mild conditions. Various functional groups were tolerated and the yields were from moderate to excellent.

1. Introduction

Palladium-catalyzed carbonylation of aryl and benzyl halides was pioneered by Heck and co-workers in 1970s and is an efficient way to prepare carboxylic acid derivatives. [1–13] Based on the mechanistic studies reported so far,[14–16] it is generally accepted that alkoxycarbonylation of aryl halides with CO proceeds through the following steps (Fig. 1): oxidative addition of an aryl halide (ArX) to Pd(0)Ln (**I**) to form intermediate ArPd(II)XLn (**II**); coordination of CO to the Pd-center and insertion into the Pd–Ar bond to give acyl palladium **IV**; reaction of **IV** with base and alcohol to release product ArCOOR and regenerate the Pd(0) catalyst.

CO is a good π-acid ligand, [17] so its coordination to Pd(0)-species will decrease the electron density in the Pd-center and make the oxidative addition step (**I**→**II**) difficult. [18] Also, because ArPd(II)XLn (**II**) is electron-deficient species, coordination of CO to **II** is more reluctant compared with that to **I**. As a result, high pressure of CO is often needed to facilitate the formation of **III**. However, high concentration of CO might further slow down the oxidative addition step (**I**→**II**) (vide supra). Thus, elevated temperature, usually higher than 100 °C, is necessary. The harsh conditions result in several problems, such as agglomeration of Pd atoms and formation of clusters, which deactivate the catalyst,[19–21] and inconvenience of application in laboratory synthesis as a routine process when high pressure apparatus are not available or substrates sensitive to high temperature are involved.

Thiourea type ligands, usually insensitive to air and moisture, have been reported to be beneficial in CO involved reactions. [22–26]

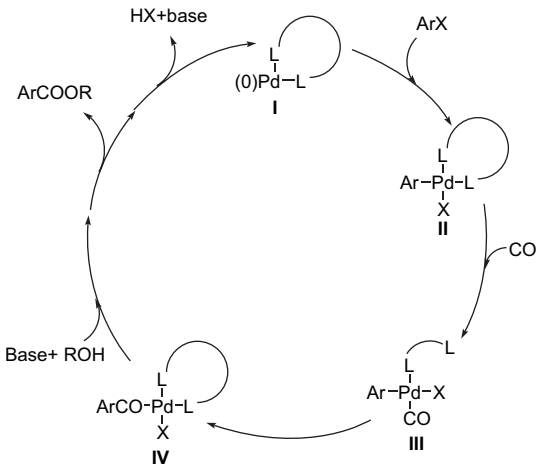

Figure 1. Proposed mechanism of Pd-catalyzed alkoxycarbonylation of aryl halides.

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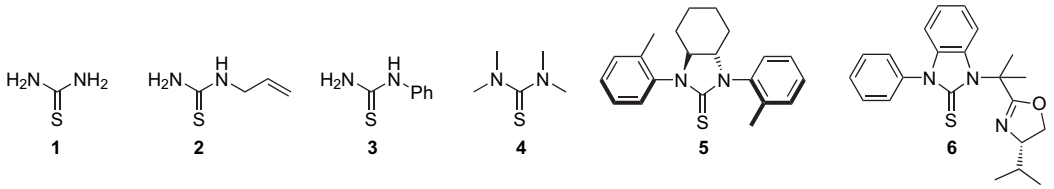


Figure 2. Different thiourea type ligands.

Recently, we have investigated palladium-catalyzed dicarboxylation reaction of olefins with this type of ligands, and achieved moderate to excellent yields under mild conditions. [27] We speculate that thioureas might be able to tune the electronic properties of the Pd(II)-species by electron resonance from the nitrogen atoms in the backbone of the ligand to the metal center, which might help the coordination of CO to the Pd(II)-species to form intermediate **III**, and finally facilitate the carbonylation of aryl halides with CO. These important features, together with the unique capability of thiourea ligands to stabilize palladium catalysts[28–36] inspired us to investigate the application of thiourea type ligands in Pd-catalyzed alkoxycarbonylation of aryl halides. We report herein our recent exploration in this important reaction.

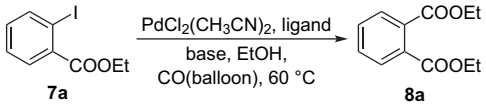
2. Result and discussion

Commercial available monodentate thiourea ligands **1**–**4** and ligands **5** and **6**[27,37] developed by our laboratory were taken for initial studies (Fig. 2). The model reaction involved ethyl *o*-iodobenzoate as the electrophile and 2 mol % palladium as the catalyst at 60 °C under balloon pressure of CO. We firstly identified that base was necessary in this transformation (Table 1, entry 1). [38] When triethylamine was used, the reaction catalyzed by $PdCl_2(CH_3CN)_2$ afforded the desired product in 77% yield (Table 1, entry 2). Then several thiourea ligands were tested. Monothioureas **1**–**5** (Fig. 2) lowered the reaction yields (Table 1, entries 3–7), while bidentate thiourea-oxazoline ligand **6** improved the yield to 99% (Table 1, entry 8). Other bases such as K_2CO_3, DBU, and DABCO afforded moderate to good yields (Table 1, entries 10–12), and sodium ethoxide furnished almost quantitative product in 3 h (Table 1, entry 9), much faster than the 24 h needed when NEt_3 was the base.

When the catalyst loading was lowered to 0.5 mol % with sodium ethoxide as the base, the reaction of ethyl *o*-iodobenzoate was completed in 6 h, and the isolated yield was 79% (Table 2, entry 1). Further lowering the catalyst loading to 0.1 mol % resulted in 57% product within 20 h (Table 2, entry 2). However, when *p*-iodoanisole was treated under the same condition, the conversion was 100%, but there was only 8% of the desired product together with 44% of anisole as the side product (detected by GC).[39] Lowering the temperature to 25 °C improved the yield to 59% (Table 2, entry 3). Two more substrates, *p*-methyliodobenzene and ethyl *p*-iodobenzoate were tested at room temperature, and only 38 and 58% products were obtained, respectively (Table 2, entries 4 and 5).

When the ethoxycarbonylation of *p*-iodoanisole was carried out in unpurified ethanol with NEt_3 as the base, 65% of ethyl *p*-methoxybenzoate was isolated with 85% conversion after 24 h, and trace anisole was detected (Table 3, entry 1). Thus NEt_3 was chosen as the base and the scope of this catalytic system was examined with aryl iodides bearing various functional groups.[40] The yields of different electrophiles varied from 60 to 99%. Functional groups such as alkoxy, cyano, ketone, ester, and nitryl groups were well tolerated (Table 2, entries 2, 5–8). *ortho*-Substituted substrates and 1-iodonaphthalene were also effectively converted into the corresponding carbonylative products in high yields (Table 2, entries 4 and 8). Biaryl compound 4-iodobiphenyl was effectively converted. 2-Iodothiophene only resulted in moderate yield, probably because of the volatility of the product (Table 3, entries 9 and 10). The catalyst worked better with substrates bearing electron-withdrawing groups, especially when the group was at the *ortho* position (Table 1, entry 8 vs Table 2, entry 5).

Table 1
Evaluation of ligands and bases[a]

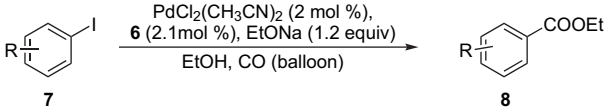


7a **8a**

Entry	Ligand	Base	Yield[b] (%)
1	—	—	0
2	—	NEt_3	77
3	**1** (4 mol %)	NEt_3	0
4	**2** (4 mol %)	NEt_3	28
5	**3** (4 mol %)	NEt_3	0
6	**4** (4 mol %)	NEt_3	35
7	**5** (4 mol %)	NEt_3	55
8	**6** (2.1 mol %)	NEt_3	99 (96[c])
9	**6** (2.1 mol %)	EtONa	98[d]
10	**6** (2.1 mol %)	K_2CO_3	56
11	**6** (2.1 mol %)	DBU	70
12	**6** (2.1 mol %)	DABCO	84

[a] Reaction conditions: $PdCl_2(CH_3CN)_2$ (2 mol %), ligand, base (1.2 equiv), **7a** (0.5 mmol), EtOH (2 mL), CO (balloon pressure), 60 °C, 24 h.
[b] GC yield determined with naphthalene as the internal standard.
[c] Isolated yield.
[d] Time: 3 h.

Table 2
Pd-**6** catalyzed ethoxycarbonylation with EtONa as the base[a]

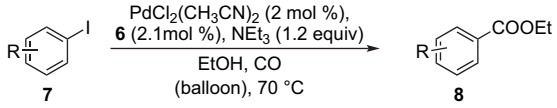


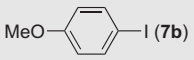
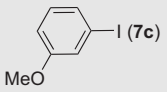
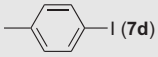
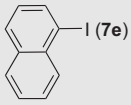
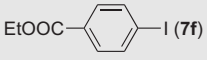
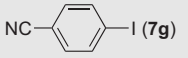
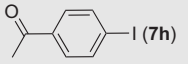
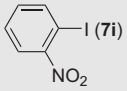
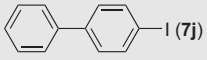
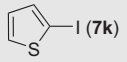
7 **8**

Entry	R	$PdCl_2(CH_3CN)_2$	**6**	Yield[b] (%)
1	*o*-COOEt	0.5 mol %	0.5 mol %	79[c]
2	*o*-COOEt	0.1 mol %	0.1 mol %	57[c]
3	*p*-OMe	2 mol %	2.1 mol %	8[c] (59[d])
4	*p*-Me	2 mol %	2.1 mol %	38[d]
5	*p*-COOEt	2 mol %	2.1 mol %	58[d]

[a] Reaction conditions: $PdCl_2(CH_3CN)_2$ (2 mol %), **6** (2.1 mol %), EtONa (1.2 equiv), **7** (0.5 mmol), EtOH (2 mL), CO (balloon pressure).
[b] Isolated yield.
[c] Temperature: 60 °C.
[d] Room temperature.

Table 3
Pd-**6** catalyzed ethoxycarbonylation with NEt_3 as the base[a]



Entry	7	Yield[b] (%)
1		65 (**8b**)
2		85 (**8c**)
3		63 (**8d**)
4		99 (**8e**)
5		91 (**8f**)
6		93 (**8g**)
7		83 (**8h**)
8		95 (**8i**)
9		99 (**8j**)
10		60 (**8k**)

[a] Reaction conditions: $PdCl_2(CH_3CN)_2$ (2 mol %), **6** (2.1 mol %), NEt_3 (1.2 equiv), **7** (0.5 mmol), EtOH (2 mL), CO (balloon pressure), 70 °C.
[b] Isolated yield.

3. Conclusion

In summary, Pd-**6** catalyst system was efficient for the ethoxycarbonylation of aryl iodides in unpurified ethanol under balloon pressure of CO with NEt_3 as the base. The protocol provides a convenient option for this type of transformation. Dehalogenated side products were detected under certain conditions. Further studies concerning the mechanism of the reactions are ongoing in our laboratory and will be reported in due course.

4. Experimental

4.1. General

Column chromatography was performed using EM silica gel 60 (230–400 mesh). ^{1}H NMR spectra were recorded on Mercury 300 MHz. All ^{1}H NMR experiments were reported in parts per million (ppm) downfield of TMS. GC–MS spectra were recorded on a Varian GC–MS 3900-2100T. Gas chromatographic analyses were performed on Varian GC 2000 gas chromatography instrument with a FID detector and naphthalene was added as the internal standard. Ethyl *o*-iodobenzoate,[41] ethyl *p*-iodobenzoate[41] and $PdCl_2(CH_3CN)_2$[42] were prepared following the literature methods. All other aryl iodides were obtained from Acros and used without further purification. Ethanol used in the reaction with sodium ethoxide as the base was distilled from magnesium and iodide. Triethylamine was used as received.

4.2. Typical procedure A

In a 10-mL Schlenk tube containing a Teflon-coated stirring bar was placed $PdCl_2(CH_3CN)_2$ (2.6 mg, 0.01 mmol), ligand **6** (4.0 mg, 0.021 mmol), and ethanol (0.5 mL) under nitrogen. The mixture was stirred at 70 °C for 10 min. Then *p*-iodoanisole **7b** (0.5 mmol) and ethanol (1.5 mL) were added successively. The system was charged with CO (balloon) and triethylamine was added by syringe. Then the system was degassed three times and held at 70 °C for 24 h with continuous stirring. After cooling to room temperature, the reaction mixture was diluted with ether (10 mL) and washed with saturated aqueous solution of NH_4Cl (5 mL). The aqueous layer was extracted with ether (3×10 mL). The combined organic phases were dried over $NaSO_4$, filtered, and concentrated. The residue was purified by a flash chromatography (PE/EtOAc=30:1) on silica gel to afford the product as a colorless oil (65%).

4.3. Typical procedure B

In a 10-mL Schlenk tube containing a Teflon-coated stir bar was placed $PdCl_2(CH_3CN)_2$ (2.6 mg, 0.01 mmol), ligand **6** (4.0 mg, 0.021 mmol), and ethanol (0.5 mL) under nitrogen. The mixture was stirred at 60 °C for 15 min. Then ethyl *o*-iodobenzoate **7a** (0.5 mmol) was added. The reaction mixture was charged with CO (balloon), followed by the addition of sodium ethoxide (1.5 mmol) in ethanol (1.5 mL). Then the system was degassed three times and stirred at 60 °C for 2 h. After cooling to room temperature, the reaction mixture was diluted with ether (10 mL) and washed with saturated NH_4Cl aqueous solution (5 mL). The aqueous layer was extracted with ether (3×10 mL). The combined organic phases were dried over $NaSO_4$, filtered, and concentrated. The residue was purified by a flash chromatography (PE/EtOAc=20:1) on silica gel to afford the product **8a** as light yellow oil (98%).

*4.3.1. Diethyl phthalate **8a***[43,44]
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79–7.67 (m, 2H), 7.60–7.48 (m, 2H), 4.37 (q, *J*=7.1 Hz, 2H), 1.37 (t, *J*=7.1 Hz, 3H).

*4.3.2. Ethyl 4-methoxybenzoate **8b***[13]
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (d, *J*=8.7 Hz, 2H), 6.91 (d, *J*=8.7 Hz, 2H), 4.35 (q, *J*=7.2 Hz, 2H), 1.38 (t, *J*=7.2 Hz, 3H).

*4.3.3. Ethyl 3-methoxybenzoate **8c***[45]
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (d, *J*=7.8 Hz, 1H), 7.57 (s, 1H), 7.34 (dd, *J*=8.1, 7.8 Hz, 1H), 7.11 (dd, *J*=8.1, 1.8 Hz, 1H), 4.38 (q, *J*=6.9 Hz, 2H), 1.40 (t, *J*=6.9 Hz, 3H).

*4.3.4. Ethyl 4-methylbenzoate **8d***[13]
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 (d, *J*=7.9 Hz, 2H), 7.08 (d, *J*=7.9 Hz, 2H), 4.23 (q, *J*=7.2 Hz, 2H), 2.25 (s, 3H), 1.25 (t, *J*=7.2 Hz, 3H).

*4.3.5. Ethyl 1-naphthoate **8e***[43]
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.92 (d, *J*=8.4 Hz, 1H), 8.16 (d, *J*=7.2 Hz, 1H), 7.97 (d, *J*=8.1 Hz, 1H), 7.84 (d, *J*=8.1 Hz, 1H), 7.59 (t, *J*=7.2 Hz, 1H), 7.52–7.43 (m, 2H), 4.45 (q, *J*=7.2 Hz, 2H), 1.43 (t, *J*=7.2 Hz, 3H).

*4.3.6. Diethyl terephthalate **8f***[12]
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (s, 4H), 4.40 (q, *J*=7.2 Hz, 2H), 1.41 (t, *J*=7.2 Hz, 3H).

4.3.7. Ethyl 4-cyanobenzoate ***8g***[46]

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15 (d, J=6.8 Hz, 2H), 7.75 (d, J=6.8 Hz, 2H), 4.42 (q, J=7.2 Hz, 2H), 1.41 (t, J=7.2 Hz, 3H).

4.3.8. Ethyl 4-acetylbenzoate ***8h***[13]

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.13 (d, J=7.8 Hz, 2H), 8.01 (d, J=7.8 Hz, 2H), 4.41 (q, J=6.9 Hz, 2H), 2.65 (s, 3H), 1.42 (t, J=6.9 Hz, 3H).

4.3.9. Ethyl 2-nitrobenzoate ***8i***[47]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92 (d, J=7.5 Hz, 1H), 7.76 (d, J=7.2 Hz, 1H), 7.71–7.61 (m, 2H), 4.40 (q, J=7.2 Hz, 2H), 1.36 (t, J=7.2 Hz, 3H).

4.3.10. Ethyl biphenyl-4-carboxylate ***8j***[48]

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11 (d, J=8.7 Hz, 2H), 7.64 (t, J=8.8 Hz, 4H), 7.47 (t, J=7.2 Hz, 2H), 7.40 (m, 1H), 4.40 (q, J=7.2 Hz, 2H), 1.42 (t, J=7.2 Hz, 3H).

4.3.11. Ethyl thiophene-2-carboxylate ***8k***[47]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80 (d, J=3.0 Hz, 1H), 7.55 (d, J=4.5 Hz, 1H), 7.10 (dd, J=3.0, 4.5 Hz, 1H), 4.36 (q, J=7.2 Hz, 2H), 1.38 (t, J=7.2 Hz, 3H).

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.07.053.

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39. *Note*. The dehalogenated side product might come from the following reactions: XPdAr+EtONa→(EtO)PdAr+NaX; (EtO)PdAr→HPdAr+CH_3CHO; HPdAr→ArH+Pd.
40. Aryl bromides were not suitable substrates and no reaction occurred when bromobenzene or ethyl 2-bromobenzoate was treated under the reaction conditions.
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