A Novel Thiourea Ligand Applied in the Pd-Catalyzed Heck, Suzuki and Suzuki Carbonylative Reactions

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Abstract: A novel C_2 symmetrical and sterically bulky thiourea ligand **1** has been successfully applied to Heck, Suzuki and Suzuki-type carbonylative coupling reactions under aerobic conditions. Since the metal-sulfur bond in the thiourea complexes is stronger than the metal-phosphorus bond of typical phosphine complexes, thiourea ligands generally do not easily dissociate from the metal center under catalytic conditions, which establishes the thiourea **1**-based palladium complexes as effective catalysts for the palladium-catalyzed cross-coupling reactions.

Keywords: cross-coupling; Heck reaction; palladium; Suzuki reaction; thiourea

The Pd-catalyzed cross-coupling reaction is a well-known method for C–C bond formation. In this context, the design of novel ligands and transition metal catalysts that can affect desired transformations with both high efficiency and high selectivity has been a fertile area of research.[1] Phosphine-based ligands have played very important roles in the Pd-catalyzed cross-coupling reactions. However these ligands usually need to be handled in an inert atmosphere or in dry conditions, and sometimes suffer from significant P–C bond degradation at elevated temperatures, which leads to palladium aggregation and affects the catalytic activity.

Recently, phosphine-free ligands, such as N-heterocyclic carbenes,[2] and sulfur-containing ligands[3] have been applied in some metal-catalyzed synthetic transformations, which open up new opportunities in catalysis.

Thioureas are compounds that are stable in air and moisture, and are renowned for their great tunability by varying substituents on the nitrogen,[4] and they can coordinate to metal centers in either the neutral state or as monoanion or dianion forms.[5] Therefore, their physical and chemical properties can be changed by modifying their nitrogen substituents.[6]

We recently reported that our newly synthesized thiourea **1** (Figure 1) can be effectively utilized in the Pd-catalyzed bismethoxycarbonylation of styrene and the cross-coupling reaction of diazonium salts and boronic acids under *oxygen*[7a] *and aerobic conditions.*[7b] Additional work to define the scope and limitations of thiourea **1** in a broad spectrum of reactions is imperative. To this end, three types of coupling reactions have now been profiled, and the details are described herein.

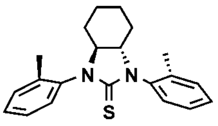
1

Figure 1. The structure of thiourea **1**.

The first reaction investigated was the Suzuki coupling because of its usefulness for C–C bond formation.[8] Considerable effort has been made to develop catalyst systems that facilitate the cross-coupling and expand its scope.[9] However, most Suzuki couplings need degassed solvents, and the reactions have to be carried out under in an inert atmosphere.[10] For this particular reason, we tested the Suzuki coupling under aerobic conditions with a thiourea **1**-ligated palladium catalyst in consideration of its beneficial air- and moisture-stability.

To this end, seven aryl iodides together with six arylboronic acids were selected for the coupling reactions with PdI_2/thiourea **1** as catalyst. As expected, good to excellent yields of coupling products were obtained under aerobic

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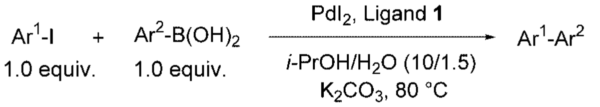
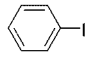
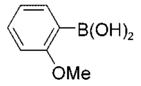
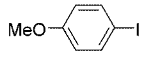
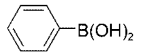
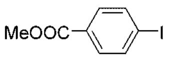
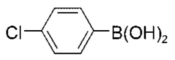
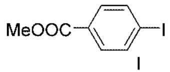
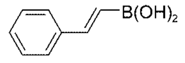
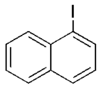
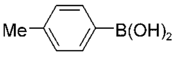
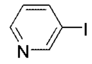
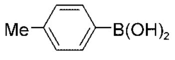
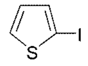
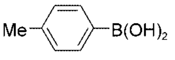
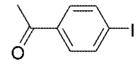
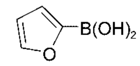
Table 1. Suzuki reaction of iodides with boronic acids.[a]



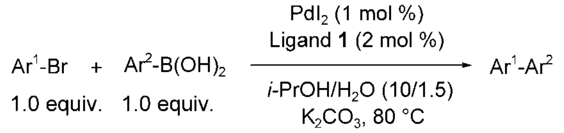
$$\underset{1.0\ \text{equiv.}}{Ar^1\text{-}I} + \underset{1.0\ \text{equiv.}}{Ar^2\text{-}B(OH)_2} \xrightarrow[\substack{i\text{-PrOH}/H_2O\ (10/1.5)\\ K_2CO_3,\ 80\ °C}]{PdI_2,\ \text{Ligand } \mathbf{1}} Ar^1\text{-}Ar^2$$

Entry	Iodide	Boronic acid	Product	Yield [%][b]
1			**1a**	97
2			**2a**	99
3			**3a**	72
4			**4a**	96
5			**5a**	98
6			**6a**	95
7			**7a**	93
8			**8a**	90

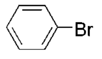
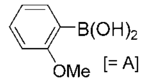
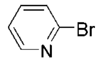
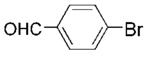
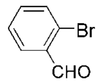
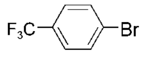
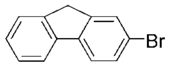
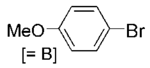
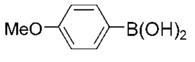
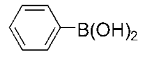
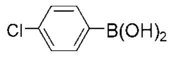
[a] Reactions between arylboronic acid (1.0 mmol), aryl iodide (1.0 mmol) and base K_2CO_3 (3.0 mmol) carried out at 80 °C for 5 hours in the presence of PdI_2 (1 mol %), ligand **1** (2 mol %) and solvent (10 mL).

[b] Isolated yield after silica gel chromatography.

Table 2. Suzuki reaction of bromides with boronic acids.



$$\underset{1.0\ \text{equiv.}}{Ar^1\text{-}Br} + \underset{1.0\ \text{equiv.}}{Ar^2\text{-}B(OH)_2} \xrightarrow[\substack{i\text{-PrOH}/H_2O\ (10/1.5)\\ K_2CO_3,\ 80\ °C}]{\substack{PdI_2\ (1\ \text{mol }\%)\\ \text{Ligand } \mathbf{1}\ (2\ \text{mol }\%)}} Ar^1\text{-}Ar^2$$

Entry	Bromide	Boronic acid	Product	Yield [%][a]
1		 [= A]	**1b**	87
2		**A**	**2b**	70
3		**A**	**3b**	99
4		**A**	**4b**	92
5		**A**	**5b**	96
6		**A**	**6b**	98
7	 [= B]	**A**	**7b**	91
8	**B**		**8b**	88
9	**B**		**9b**	98
10	**B**		**10b**	70

[a] Isolated yield after silica gel chromatography.

conditions, and the results are shown in Table 1. Interestingly, in these coupling reactions, the ratio of PdI_2 to thiourea **1** (1:2) is an important parameter to achieve good results, changing the ratio led to decreased yields.

We then ran similar reactions with the less reactive aryl bromides with boronic acids. To our delight, all reactions worked well under the conditions listed in Table 2, both electron-poor and electron-rich aryl bromides gave similar results under aerobic conditions.

The metal-catalyzed three-component reaction with arylmetal (B, Zn, Cu, Al, Si, In),[11] carbon monoxide (CO), and aryl electrophile is a valuable method for the synthesis of unsymmetrical ketones as opposed to the Lewis acid-catalyzed Friedel–Crafts acylation. However, one problem associated with this reaction is the formation of a significant amount of biaryl products when electron-deficient aryl halides were used, presumably because the halides react too quickly with arylmetals without insertion of CO.[11m]

Miyaura and co-workers have resolved this issue by applying CO at higher pressures to get the high yields of coupling products.[11m] Andrus and co-workers recently achieved good yields by the imidazolium-based Pd-catalyzed coupling of diazonium salts and boronic acids at 1 atm CO.[11s] The beneficial effect of thiourea **1** to incorporate CO into the palladium complex in our previous study of the bismethoxycarbonylation of styrene[7b] prompted us to apply thiourea **1** to this unsymmetrical ketone synthesis.

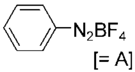
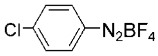
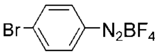
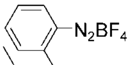
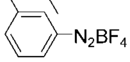
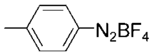
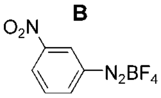
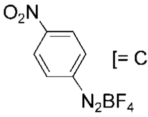
Thus, eight diazonium salts were reacted with several arylboronic acids under the conditions listed in Table 3. Fortunately, all substrates gave the desired products. However, the nitro-based salts (see entries 17–23) gave lower yields than Andrus' method.[11s] It should be noted that only trace amounts of biaryl coupling products were obtained in most of our coupling reactions, which indicated the favorable effect of thiourea **1** in the Pd-catalyzed carbonylative reaction.

To further extend the scope of these carbonylative reactions, aryl iodides were reacted with boronic acids in anisole[12a] at 80 °C under balloon pressure of CO, and better results were obtained (see Table 4).

Our final investigation was the Heck coupling. When the active aryl iodides were reacted with methyl acrylate, good to excellent yields of coupling products were obtained (see Table 5). But no desired products were generated when the less active aryl bromides were applied in this reaction.

Table 3. Suzuki-carbonylative reaction of diazonium salts with arylboronic acids.

$$\underset{1.0\ \text{equiv.}}{Ar^1N_2BF_4} + \underset{1.0\ \text{equiv.}}{Ar^2B(OH)_2} \xrightarrow[\text{THF, CO, 10 h}]{\text{Pd(OAc)}_2\text{, Ligand } \mathbf{1}} Ar^1COAr^2$$

Entry	Diazonium salt	Boronic acid	Product	Yield [%][c]
1	 [= A]	*p*-MeO-C_6H_4-$B(OH)_2$	**1c**	87[a]
2	**A**	*o*-MeO-C_6H_4-$B(OH)_2$	**2c**	70[a]
3	**A**	*p*-Me-C_6H_4-$B(OH)_2$	**3c**	72[a]
4	**A**	*o*-Me-C_6H_4-$B(OH)_2$	**4c**	76[a]
5	**A**	*p*-Cl-C_6H_4-$B(OH)_2$	**5c**	65[a]
6	**A**	Ph-$B(OH)_2$	**6c**	66[a]
7		Ph-$B(OH)_2$	**5c**	69[a]
8		Ph-$B(OH)_2$	**7c**	73[a]
9		Ph-$B(OH)_2$	**4c**	30[a]
10		Ph-$B(OH)_2$	**8c**	62[a]
11	 [= B]	*p*-MeO-C_6H_4-$B(OH)_2$	**9c**	80[a]
12	**B**	*o*-MeO-C_6H_4-$B(OH)_2$	**10c**	74[a]
13	**B**	*p*-Me-C_6H_4-$B(OH)_2$	**11c**	70[a]
14	**B**	*o*-Me-C_6H_4-$B(OH)_2$	**12c**	74[a]
15	**B**	*p*-Cl-C_6H_4-$B(OH)_2$	**13c**	73[a]
16	**B**	Ph-$B(OH)_2$	**3c**	79[a]
17		Ph-$B(OH)_2$	**14c**	70[a]
18	 [= C]	*p*-MeO-C_6H_4-$B(OH)_2$	**15c**	76[b]
19	**C**	*o*-MeO-C_6H_4-$B(OH)_2$	**16c**	81[b]
20	**C**	*p*-Me-C_6H_4-$B(OH)_2$	**17c**	80[b]
21	**C**	*o*-Me-C_6H_4-$B(OH)_2$	**18c**	88[b]
22	**C**	*p*-Cl-C_6H_4-$B(OH)_2$	**19c**	72[b]
23	**C**	Ph-$B(OH)_2$	**20c**	70[b]

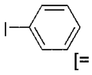
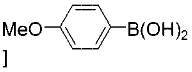
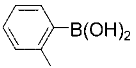
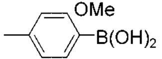
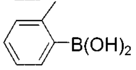
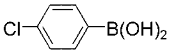
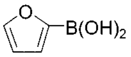
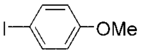
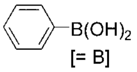
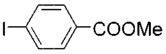
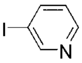
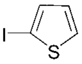
[a] Reactions between arylboronic acid (1.0 mmol), CO (balloon pressure), and diazonium salt (1.0 mmol) were carried out at 50 °C for 10 hours in the presence of $Pd(OAc)_2$ (2 mol %), ligand **1** (2 mol %) and solvent (10 mL).

[b] Reactions between arylboronic acid (1.0 mmol), CO (balloon pressure), and diazonium salt (1.0 mmol) were carried out at 20 °C for 10 hours in the presence of $Pd(OAc)_2$ (5 mol %), ligand **1** (2 mol %) and solvent (10 mL).

[c] Isolated yield after silica gel chromatography.

Table 4. Suzuki carbonylative reaction of aryl iodides with arylboronic acids.

$$\underset{1.0\ \text{equiv.}}{Ar'I} + \underset{1.0\ \text{equiv.}}{ArB(OH)_2} \xrightarrow[\substack{\text{Anisole, } K_2CO_3 \\ 80\ ^\circ\text{C, CO}}]{\text{Pd(OAc)}_2\text{, Ligand } \mathbf{1}} Ar'COAr$$

Entry	Aryl iodide	Boronic acid	Product	Yield [%][a]
1	 [= A]		**1c**	94
2	**A**		**2c**	70
3	**A**		**3c**	98
4	**A**		**4c**	84
5	**A**		**5c**	89
6	**A**		**1d**	89
7		 [= B]	**1c**	92
8		**B**	**2d**	97
9		**B**	**3d**	90
10		**B**	**4d**	88

[a] Isolated yield after silica gel chromatography.

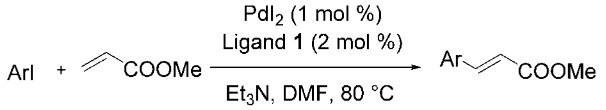
In summary, we have illustrated the utilization of our newly synthesized thiourea **1** in a variety of Pd-catalyzed cross-coupling reactions, and satisfactory results were obtained. In consideration of its thermal stability, insensitivity to air and moisture, and tunability by modifying its nitrogen substituents, thiourea **1** is worthy of further investigation.

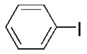
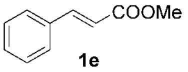
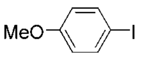
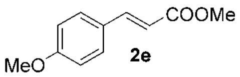
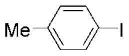
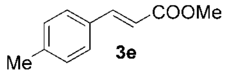
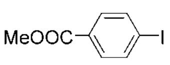
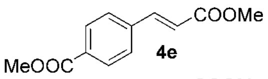
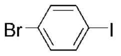
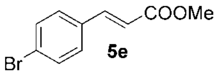
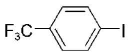
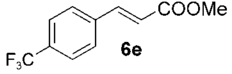
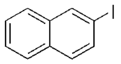
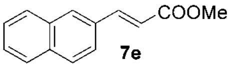
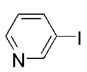
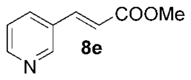
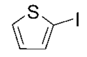
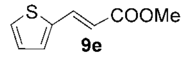
Experimental Section

General Information

All reagents were purchased from Aldrich and used without further purification. All solvents were distilled prior to use. The boiling point of petroleum ether is between 60–90 °C. Silica gel (200–300 mesh) for purification was purchased from Qing Dao Hai Yang Chemical Industry Co. of China. ^1H NMR and ^{13}C NMR were recorded at 300 MHz and 75 MHz with a Varian Mercury 300 spectrometer or at 400 MHz and 100.6 MHz with a Bruker ARX400 spectrometer. Mass spectrometric data were obtained using a ZAB-HS mass spectrometer. The purity of the synthesized compounds was checked by ^1H and ^{13}C NMR spectroscopy.

Table 5. Heck cross-coupling reaction of aryl iodides with methyl acrylate.[a]



Entry	Iodide	Product	Yield [%][b]
1		 **1e**	96
2		 **2e**	98
3		 **3e**	85
4		 **4e**	73
5		 **5e**	98
6		 **6e**	92
7		 **7e**	89
8		 **8e**	85
9		 **9e**	95

[a] Reactions between methyl acrylate (1.2 mmol), aryl iodide (1.0 mmol) and Et_3N (3.0 mmol) carried out at 80 °C for 5 hours in the presence of PdI_2 (1 mol %), ligand **1** (2 mol %) and DMF (10 mL).

[b] Isolated yield after silica gel chromatography.

General Procedure for the Synthesis of Biaryl Compounds by Coupling of Aryl Iodides or Bromides and Arylboronic Acid (1a–8a, and 1b–10b)

Aryl iodides or bromides (1.0 mmol), arylboronic acid (1.0 mmol), K_2CO_3 (3.0 mol), PdI_2 (0.015 mmol, 1.5 mol %) and thiourea 1 (0.03 mmol, 3 mol %) were mixed in isopropyl alcohol/H_2O (10 mL/1.5 mL) under aerobic conditions, and the reaction mixture was stirred at 80 °C for 5 hours. The reaction mixture was first passed through a silica gel plug, and then washed with ethyl acetate. The filtrate was concentrated under vacuum and the residue was purified by flash chromatography on silica gel.

General Procedure for the Syntheses of Unsymmetrical Aryl Ketones by the Carbonylative Coupling of Aryldiazonium Salts with Arylboronic Acids (1c–20c)

Aryldiazonium tetrafluoroborate (1.0 mmol), arylboronic acid (1.0 mmol), $Pd(OAc)_2$ (0.02 mmol, 2 mol %) and thiourea **1** (0.02 mmol, 2 mol %) were mixed under nitrogen in a round-bottom flask. Anhydrous THF (10 mL) was added and the flask was charged with CO (balloon), and the reaction mixture was stirred at 50 °C for 10 hours. The reaction mixture was worked up by removing the solvent under vacuum and the residue was purified by a flash chromatography on silica gel.

General Procedure for the Syntheses of Unsymmetrical Ketones by the Carbonylative Coupling of Aryl Iodide with Arylboronic Acid (1d–4d)

Aryl iodide (1.0 mmol), arylboronic acid (1.0 mmol), K_2CO_3 (3.0 mmol), PdI_2 (0.01 mmol, 1 mol %) and thiourea **1** (0.02 mmol, 2 mol %) were mixed in anhydrous anisole (10 mL) under balloon pressure of CO, and the reaction mixture was stirred at 80 °C for 10 hours. The reaction mixture was worked up by removing the solvent under vacuum and the residue was purified by flash chromatography on silica gel.

General Procedure for the Synthesis of Compounds 1e–9e by Coupling of Aryl Halides and Methyl Acrylate

Aryl iodides (1.0 mmol), methyl acrylate (1.2 mmol), Et_3N (3.0 mmol), PdI_2 (0.01 mmol, 1.0 mol %) and thiourea **1** (0.02 mmol, 2.0 mol %) were mixed in DMF (10 mL), and the reaction mixture was stirred at 80 °C for 5 hours under aerobic conditions. The reaction was worked up by extraction of the reaction mixture with ethyl acetate, washed with saturated NaCl solution, and dried over Na_2SO_4. After removing the solvent under vacuum, the residue was purified by flash chromatography on silica gel.

Acknowledgements

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