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Phosphine-Free Hydrazone−Pd Complex as the Catalyst Precursor for a Suzuki−Miyaura Reaction under Mild Aerobic Conditions

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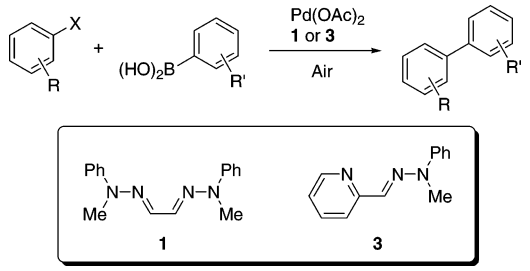

Glyoxal bis(*N*-methyl-*N*-phenylhydrazone) (**1**) and its related compounds such as 2-pyridinecarboxaldehyde *N*-methyl-*N*-phenylhydrazone (**3**) were prepared and examined as ligands for the Suzuki−Miyaura cross-coupling reaction of aryl halides and arylboronic acids. We found phosphine-free catalysts, such as $Pd(OAc)_2$/hydrazone ligand **1** or **3**, to be efficient catalysts for a variety of substrates to produce the coupling products in good yields.

Introduction

The palladium-catalyzed Suzuki−Miyaura cross-coupling reaction of aryl halides with arylboronic acids and esters has become a common and convenient synthetic method in organic chemistry for biaryl compounds.[1] The reaction has been applied to many areas,[2] including natural product synthesis.[3] Triarylphosphine/Pd complexes are commonly used as catalysts for the reaction.[1a] In the past few years, great advances have been made in developing active and efficient catalysts by modifying traditional ligands and discovering new ones. Sterically demanding, electron-rich phosphines, such as tri-*tert*-butylphosphine, have shown high cross-coupling activities for a variety of substrates.[4] In the meantime, new types of ligands, such as heterocyclic carbenes,[5] imine and amine palladacycles,[6] oxime palladacycles,[7] diazabutadienes,[8] 2-aryl-2-oxazolines,[9] and simple amines,[10] have also emerged for use in the Suzuki−Miyaura cross-coupling reaction.

The synthesis and properties of palladium complexes with hydrazone ligands have been previously reported,[11]

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(4) (a) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **1998**, *37*, 3387. (b) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020.

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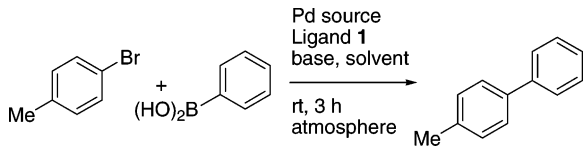
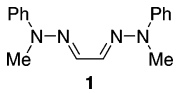
TABLE 1. Optimization of Reaction Conditions at Room Temperature[a]



entry	base	solvent	Pd source	yield (%)[b]
1	$Ca(OH)_2$	DMF	$Pd(OAc)_2$	59
2	Na_2CO_3	DMF	$Pd(OAc)_2$	53
3	K_2CO_3	DMF	$Pd(OAc)_2$	73
4	Cs_2CO_3	DMF	$Pd(OAc)_2$	88
5	CsF	DMF	$Pd(OAc)_2$	42
6	Cs_2CO_3	1,4-dioxane	$Pd(OAc)_2$	33
7	Cs_2CO_3	THF	$Pd(OAc)_2$	48
8	Cs_2CO_3	PhMe	$Pd(OAc)_2$	41
9	Cs_2CO_3	DMSO	$Pd(OAc)_2$	5
10	Cs_2CO_3	DMAc	$Pd(OAc)_2$	59
11	Cs_2CO_3	DMF−H_2O[c]	$Pd(OAc)_2$	99[d]
12	Cs_2CO_3	DMF−H_2O[c]	$PdCl_2$	92[d]
13	Cs_2CO_3	DMF−H_2O[c]	$PdCl_2(MeCN)_2$	59[d]
14[e]	Cs_2CO_3	DMF−H_2O[c]	$Pd(OAc)_2$	99[d]

[a] Reaction conditions: 4-bromotoluene (1 mmol), phenylboronic acid (1.5 mmol), base (2 mmol), solvent (3 mL), Pd-source (0.02 mmol), ligand **1** (0.03 mmol), 3 h. [b] GLC yields (2-methoxynaphthalene as internal standard; an average of two runs). [c] The mixture of DMF (2 mL) and H_2O (1 mL) was used as a solvent. [d] Isolated yields. [e] This reaction was carried out under Ar.

and we expect hydrazone ligands to have advantages over phosphine ligands due to their ease of synthesis and air stability. We report here the Suzuki−Miyaura cross-coupling reaction using glyoxal bis(*N*-methyl-*N*-phenylhydrazone) (**1**) as a ligand of catalyst precursor.[12]

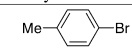
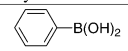
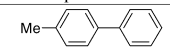
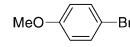
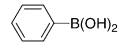
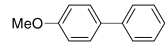
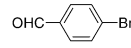
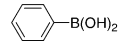
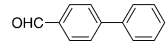
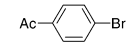
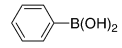
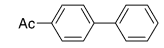
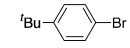
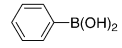
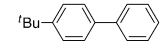
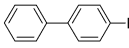
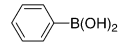
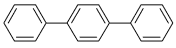
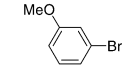
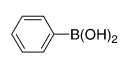
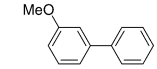
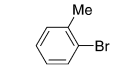
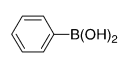
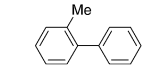
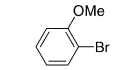
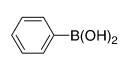
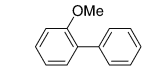
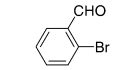
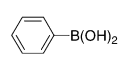
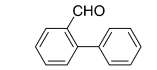
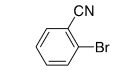
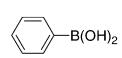
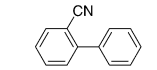
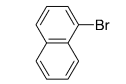
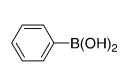
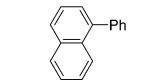
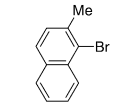


1

Results and Discussion

Optimization of Reaction Conditions. Glyoxal bis(methylphenylhydrazone) (**1**) was easily prepared from glyoxal and 2 equiv of *N*-methyl-*N*-phenylhydrazine in methanol. Using this hydrazone **1** as ligand, we applied the coupling of 4-bromotoluene and phenylboronic acid in the presence of $Pd(OAc)_2$ under an aerobic atmosphere at room temperature for finding out the optimum reaction conditions (Table 1). The use of cesium carbonate as a base led to higher yield for this reaction (entry 4 vs entries 1−3 and 5). In the presence of cesium carbonate, many commonly used solvents were tested (entries 4 and 6−10). The etheral solvents such as dioxane and THF or nonpolar solvent toluene were not effective (entries 6−8). The DMF−water system was preferred for this reaction (entry 4 vs entry 11). Other palladium catalysts proved to be less effective in this reaction (entries 12 and 13).

TABLE 2. Suzuki−Miyaura Reaction of Aryl Bromide with Arylboronic Acid at Room Temperature under Aerobic Conditions[a]

entry	aryl bromide	arylboronic acid	product	yield (%)[b]
1[c]				99
2				89
3				99
4				99
5				94
6				88
7				91
8				90
9				89
10				87
11				88
12				92
13				24
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20[e]				94
21[e]				83

[a] Reaction conditions: aryl bromide (1 mmol), phenylboronic acid (1.5 mmol), $Pd(OAc)_2$ (2 mol %), ligand **1** (3 mmol %), Cs_2CO_3 (2 mmol), DMF (2 mL), H_2O (1 mL), rt, 3 h. [b] Isolated yield. [c] This reaction was carried out in 30 min. [d] This reaction was carried out with 4 mol % of $Pd(OAc)_2$ and 6 mol % of ligand **1** in 50 h. [e] This reaction was carried out with 4 mol % of $Pd(OAc)_2$ and 6 mol % of ligand **1** in 24 h.

Under argon atmosphere with the $Pd(OAc)_2$/hydrazone **1** system, the reaction also proceeded to 99% at room temperature (entry 14).

Suzuki−Miyaura Reaction at Room Temperature under Aerobic Conditions. The effect of varying the aryl bromide in the Suzuki−Miyaura reactions was investigated by using phenylboronic acid as the substrate at room temperature (Table 2). Using 4-substituted and 3-substituted aryl bromides led to good yields of the

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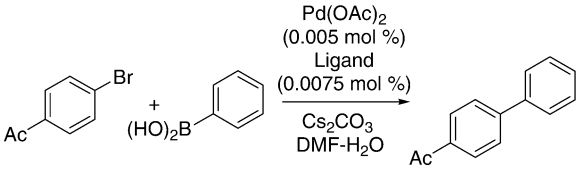
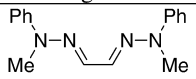
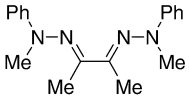
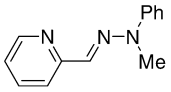
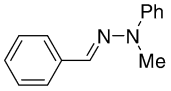
TABLE 3. Effect of Ligand under Low Catalyst Loading Suzuki−Miyaura Reaction at Room Temperature under Aerobic Conditions[a]



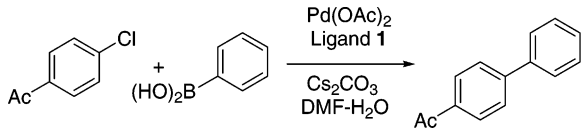
entry	ligand	time (h)	yield(%)[b]
1	 **1**	24	89
2	 **2**	24	39
3	 **3**	24	99
4		3	83
5	 **4**	24	63

[a] Reaction conditions: 4-Ac-PhBr (1 mmol), phenylboronic acid (1.5 mmol), $Pd(OAc)_2$ (0.00005 mmol), ligand (0.000075 mmol), Cs_2CO_3 (2 mmol), DMF (2 mL), H_2O (1 mL), rt. [b] Determined by ^1H NMR with 2-methoxynaphthalene as internal standard.

desired products (entries 1−7). Moreover, 2-substituted aryl bromide and 1-bromonaphthalene also led to good yields (entries 8−12). The reaction of 1-bromo-2-methylnaphthalene with phenylboronic acid resulted in a low yield (entry 13). The effect of varying the arylboronic acids was also investigated by using 4-bromotoluene as the substrate at room temperature (entries 14−18). Using 4-substituted arylboronic acids led to moderate to good yields of the desired products (entries 14 and 15). 2-Fluorophenylboronic acid and 1-naphthaleneboronic acid also led to good yields (entries 16 and 18), but 2-formylphenylboronic acid led to a low yield (entry 17). In addition to substituted aryl bromides, the reactions with heterocyclic bromides led to the formation of the desired products in moderate to good yields (entries 19−21).

Low Catalyst Loading Suzuki−Miyaura Reaction. Under low catalyst loadings with the $Pd(OAc)_2$/hydrazone **1** system (0.005 mol % Pd) (Table 3, entry 1), it was necessary to use longer reaction times such as 24 h. We investigated the effect of ligand in the Suzuki−Miyaura reaction of 4′-bromoacetophenone and phenylboronic acid at room temperature. The reaction with bishydrazone **2** prepared from 2,3-butanedione resulted in a low yield (entry 2). On the other hand, similar monohydrazone type ligand **3** gave a quantitative yield with high turnover number (TON = 19 800) after 24 h (entry 3). Under the same conditions the desired product was obtained in high yield with high turnover frequency (TOF = 5533 h^{-1}) in only 3 h (entry 4). When the reaction was carried out with ligand **4**, a poor result was obtained (entry 5).

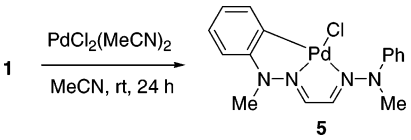
TABLE 4. Suzuki−Miyaura Reaction of 4′-Chloroacetophenone with Phenylboronic Acid under Aerobic Conditions[a]



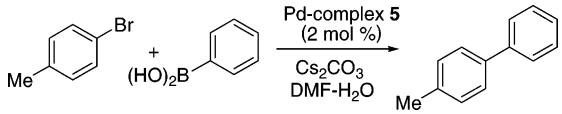
entry	Pd source/ligand	temp (°C)/time (h)	yield (%)[b]
1	$Pd(OAc)_2$ (4 mol %) **1** (6 mol %)	100/48	67
2	$Pd(OAc)_2$ (10 mol %) **1** (15 mol %)	100/8	66
3	$Pd(OAc)_2$ (10 mol %) **3** (15 mol %)	100/8	35

[a] Reaction conditions: 4-Ac-PhCl (1 mmol), phenylboronic acid (1.5 mmol), $Pd(OAc)_2$, ligand, Cs_2CO_3 (2 mmol), DMF (2 mL), H_2O (1 mL). [b] Isolated yield.

SCHEME 1. Preparation of Palladium Complex 5



SCHEME 2. Suzuki−Miyaura Reaction with 5 as a Catalyst



Suzuki−Miyaura Reaction of Aryl Chloride. We also attempted the coupling of 4′-chloroacetophenone and phenylboronic acid in the presence of 4 mol % of $Pd(OAc)_2$ using ligand **1** under an aerobic atmosphere at 100 °C. It was necessary to use longer reaction times (entry 1). With 10 mol % of $Pd(OAc)_2$ the reaction gave a good yield of the desired product after 8 h (entry 2). Unfortunately ligand **3** was not effective in this reaction (entry 3).

Synthesis and Characterization of the Hydrazone−Palladium Complex. To investigate the nature of the catalyst structure, a single red crystal of the Pd-complex **5** was obtained from the reaction of glyoxal bis(methylphenylhydrazone) (**1**) and $PdCl_2(MeCN)_2$ in acetonitrile under air (Scheme 1).

X-ray analysis of **5** showed the hydrazone-derived palladacycle and the palladium atom bound to two nitrogen atoms on the ligand. Additionally, the Pd−N bonds are asymmetric with a difference of 0.262 Å. When 2 mol % of complex **5** was used as catalyst, the reaction of 4-bromotoluene and phenylboronic acid was proceeded smoothly in 99% yield for 3 h at room temperature (Scheme 2).

Conclusions

It can be concluded that the Suzuki−Miyaura reaction of aryl bromide and arylboronic acids can be performed under mild phosphine-free conditions, based on $Pd(OAc)_2$/hydrazone **1** and its related compounds with cesium carbonate in the DMF−water system under an aerobic atmosphere at room temperature. Under low catalyst loading conditions, ligand **3** gave a high turnover number

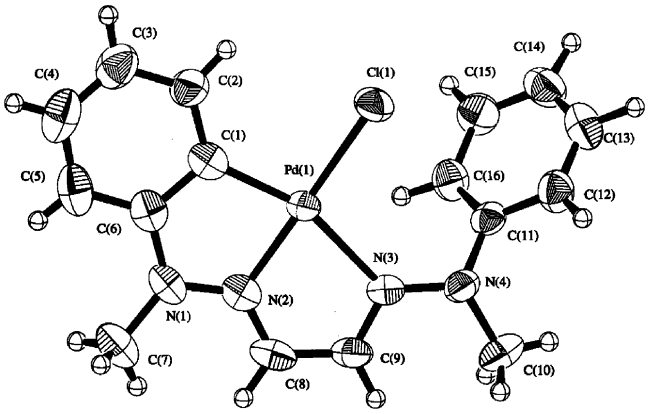


FIGURE 1. ORTEP plot of the Pd-complex **5**.

(TON = 19800) and a high turnover frequency (TOF = 5533 h^{-1}). $Pd(OAc)_2$/hydrazone **1** also shows a reactivity of the Suzuki−Miyaura reaction with aryl chloride such as that with 4′-chloroacetophenone at 100 °C.

Experimental Section

Typical Procedure for the Preparation of Ligand. A mixture of *N*-methyl-*N*-phenylhydrazine (1.22 g, 10 mmol) in MeOH (3 mL) was added to 40 wt % of glyoxal in water (0.725 g, 5 mmol) at 0 °C. The mixture was stirred for 1 h at room temperature. The yellow solid precipitated and was collected by filtration, washed with water, and dried in vacuo. Recrystallization from hexane−chloroform gave **1** as a yellow solid (0.978 g, 3.68 mmol).

Glyoxal bis(*N*-methyl-*N*-phenylhydrazone) (1): 74% yield; mp 216−217 °C; ^{1}H NMR ($CDCl_3$) δ 3.39 (s, 3H), 6.90−6.96 (m, 2H), 7.30−7.32 (m, 8H), 7.51 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 33.4, 115.6, 120.8, 129.1, 133.8, 147.6; EI-MS *m/z* (rel intensity) 266 (M^+); HRMS (FAB-MS) *m/z* calcd for $C_{16}H_{18}N_4$ 266.1531, found 266.1508.

2,3-Butanedion bis(*N*-methyl-*N*-phenylhydrazone) (2): ^{13}17% as a light yellow solid; mp 99−100 °C; ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 6H), 3.24 (s, 6H), 6.93 (tt, J = 1.0 and 7.3 Hz, 2H), 7.04 (dd, J = 1.1 and 7.7 Hz, 4H), 7.30 (t, J = 7.3 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 16.2, 43.4, 115.9, 120.8, 129.3, 151.4, 162.8; EI-MS *m/z* (rel intensity) 294 (M^+, 20).

2-Pyridinecarboxyaldehyde *N*-methyl-*N*-phenylhydrazone (3): 64% as a yellow solid; mp 67−68 °C; ^{1}H NMR ($CDCl_3$) δ 3.46 (s, 3H), 6.98 (tt, J = 1.2 and 7.0 Hz, 1H), 7.14 (ddd, J = 1.1, 1.2 and 6.1 Hz 1H), 7.29−7.45 (m, 4H), 7.61 (s, 1H), 7.68 (dt, J = 1.6 and 7.9 Hz, 1H), 8.02 (d, J = 8.1 Hz 1H), 8.53 (qt, J = 0.7 and 4.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 33.4, 115.6, 119.1, 121.3, 121.9, 129.1, 132.6, 136.2, 147.4, 149.0, 155.9; EI-MS *m/z* (rel intensity) 211 (M^+, 19); HRMS (FAB-MS) *m/z* calcd for $C_{13}H_{13}N_3$ 211.1109, found 211.1105.

Benzaldehyde *N*-methyl-*N*-phenylhydrazone (4):[14] 54% as a white solid; mp 104−105 °C; ^{1}H NMR ($CDCl_3$) δ 3.42 (s, 3H), 6.91 (t, J = 6.9 Hz, 1H), 7.24−7.40 (m, 7H), 7.49 (s, 1H), 7.69 (d, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 33.4, 115.6, 120.9, 126.4, 128.1, 129.0, 129.4, 132.2, 137.1, 148.2; EI-MS *m/z* (rel intensity) 210 (M^+, 100).

Bishydrazone-Pd-Catalyzed Suzuki−Miyaura Reaction of Aryl Bromide with Arylboronic Acid. General procedure: Under an atmosphere of air, aryl halide (1 mmol) was added to the mixture of arylboronic acid (1.5 mmol), palladium acetate (0.02 mmol), hydrazone **1** (0.03 mmol), and Cs_2CO_3 (2 mmol) in *N,N*-dimethlyformamide (DMF) (2 mL) and water (1 mL) at room temperature. The mixture was stirred and monitored by TLC. In the case of entries 1−10, Table 1, the yield was determined by GC (Shimadzu GC-14B using CPB20-m25-025 column) with 2-methoxynaphthalene as an internal standard. The mixture was diluted with ether and water. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography.

2-Methyl-1-phenylnaphthalene (Table 2, entry 13): 24% as a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 2.23 (s, 3H), 7.21−7.52 (m, 9H), 7.75−7.84 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.8, 124.8, 125.8, 126.2, 127.0, 127.2, 127.8, 128.3, 128.4, 130.2, 132.0, 132.9, 133.1, 138.2, 139.8; EI-MS *m/z* (rel intensity) 218 (M^+); HRMS (EI-MS) *m/z* calcd for $C_{17}H_{14}$ 218.1096, found 218.1107.

Preparation of Palladium Complex 5. A mixture of hydrazone **1** (0.134 g, 0.5 mmol) in acetonitrile (15 mL) was added to $PdCl_2(MeCN)_2$ (0.130 g, 0.5 mmol) and the mixture was stirred for 24 h at room temperature. The mixture was then filtered on Celite and concentrated under reduced pressure. The red solid precipitated and was collected by filtration and dried in vacuo (0.169 g, 0.41 mmol). Recrystallization from hexane−chloroform gave **5** as a red solid for X-ray analysis.

5: 82% yield; mp 170−171 °C; ^{1}H NMR (DMSO-d_6) δ 3.25 (s, 3H), 3.38 (s, 3H), 6.30−6.45 (m, 2H), 6.80−6.84 (m, 1H), 6.90−6.97 (m, 1H), 7.17−7.21 (m, 1H), 7.22−7.30 (m, 4H), 7.46−7.52 (m, 1H), 7.60−7.64 (m, 1H); ^{13}C NMR (DMSO-d_6) δ 33.3, 38.2, 108.7, 119.1, 119.3, 123.3, 125.1, 128.5, 128.9, 129.2, 135.1, 135.5, 137.3, 146.1, 152.7, 153.0; MS (FAB) *m/z* 406 (M^+); HRMS (FAB-MS) *m/z* calcd for $C_{16}H_{17}N_4{}^{35}Cl^{106}Pd$ 406.0180, found 406.0185.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of all compounds and an X-ray crystallographic file (CIF) for **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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