

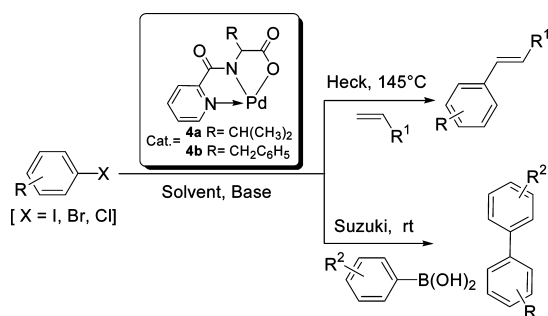
Trifunctional *N,N,O*-Terdentate Amido/Pyridyl Carboxylate Ligated Pd(II) Complexes for Heck and Suzuki Reactions

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Trifunctional *N,N,O*-terdentate amido/pyridyl carboxylate Pd(II) complexes were highly active and stable phosphine-free catalysts for Heck and room-temperature Suzuki reactions with high turnover numbers up to ca. 10⁴.

Palladium-catalyzed C–C bond-formation reactions such as the Heck and Suzuki cross-couplings have found applications in the synthesis of natural products and pharmaceuticals and materials science.¹ The great importance of C–C bond-forming reactions has encouraged the chemical community to search for highly active and stable palladium catalysts, which should be versatile and efficient.² Recently, well-designed phosphine-based ligands have contributed significantly to improving catalytic activity as a result of their increasing bulkiness and electron-

donating functionality that favors both the oxidative addition and reductive elimination steps in the catalytic cycle.³ However, phosphine-containing ligands are toxic, air-sensitive, and quite expensive. Therefore, the development of phosphine-free catalysts for C–C bond-forming reactions would be an important topic of interest.

To date, a number of phosphine-free ligands with different donor-functionalities such as *N*-heterocyclic,⁴ carbocyclic,⁵ and anionic carbocyclic⁶ carbenes, oxazolines,⁷ Schiff bases,⁸ pyridines,⁹ amines,¹⁰ imidazoles,¹¹ pyrazoles,¹² hydrazones,¹³ selenides,¹⁴ ureas,¹⁵ and thioureas¹⁶ have appeared for C–C cross-coupling reactions. Most of these ligands are mono- or bifunctional ligands. They reveal that each donor-functional group has its own characteristic nature to influence the efficacy of its palladium complex and also disclose that none of the functional groups have all of the properties that make the palladium very stable and catalytically active. Therefore, we assumed that the design and development of phosphine-free multifunctional ligands using different donor-functionalities may provide stable and well-defined active palladium catalysts.

Recently, we have reported *N4*-tetradentate dicarboxamidate/dipyridyl palladium(II) complexes as catalysts for the Heck

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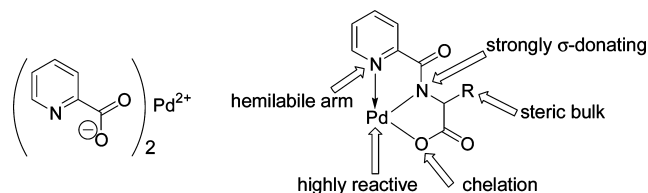
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SCHEME 1. Design of Multifunctional Pd(II) Complexes



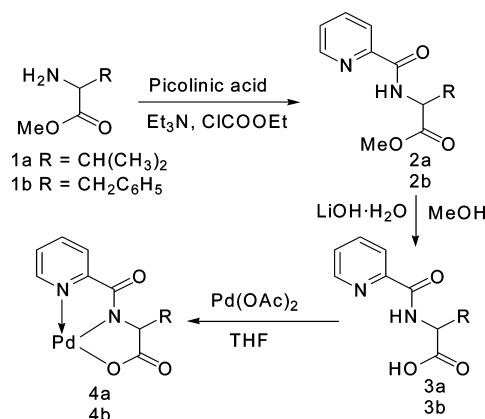
reaction of deactivated aryl chlorides.¹⁷ This was the first report on the use of purely N-donor ligands that show significant catalytic activity with deactivated aryl chlorides in the Heck reaction. It was observed that the anionic amide (deprotonated amide) ligands strongly donate electrons to the metal center, thus stabilizing the various oxidation states of the metals.¹⁸ Such ionic-type amidate bonding in palladium complexes could impart larger thermodynamic stabilization to active metal species.

As reported by Yao et al. in 2003 and demonstrated by the theoretical study of Amatore and Jutand and the coordination by anionic carboxylates could enhance the activity of Pd toward oxidative addition.¹⁹ In addition, Reetz et al. and Liu et al. have shown that alkylamine and pyridine are good neighboring groups to enhance the effect of a carboxylate group in Pd catalysis.²⁰ Owing to the impressive activity of the anionic carboxamide as an ancillary ligand in the Heck reaction,¹⁷ enhancement of the catalytic activity might be expected by introducing carboxamide into the bifunctional pyridine-2-carboxylic acid ligand as the pendant functionality (Scheme 1).

In this paper, we report the successful synthesis of palladium(II) complexes of trifunctional amido/pyridyl carboxylate ligands and their catalytic activity for the C–C bond-formation reactions. The investigation of the reactivity of the resulting trifunctional Pd(II) complexes would provide a new and efficient catalyst system for Heck and Suzuki reactions under phosphine-free conditions.

The ligands **3a** and **3b** were prepared in good yields using the method described in our previous work.¹⁷ The palladium(II) complexes (**4a** and **4b**) were prepared, in almost quantitative yields, by simple addition of *N,N,O*-terdentate ligands (**3a** and **3b**) to a orange-colored solution of Pd(OAc)₂ in tetrahydrofuran at room temperature (see Scheme 2). Complex **4a** is soluble in polar organic solvents such as CHCl₃, CH₂Cl₂, THF, MeOH, DMF, and DMSO, whereas complex **4b** is soluble only in very highly polar organic solvents such as DMSO, DMF, and DMA. Complex **4a** and **4b** have been fully characterized by spectroscopy (NMR, MS, FT-IR) and by elemental analysis. The solution structure of the palladium complexes were studied by ¹H and ¹³C NMR spectroscopy, and these studies show the presence of amidate bonding to palladium similar to that observed in our previous work. Remarkably, both palladium(II) complexes show high thermal stability up to 280 °C as analyzed

SCHEME 2. Synthesis of Amido/Pyridyl Carboxylate Palladium(II) Complexes

TABLE 1. Heck Reaction between Bromoanisole and *n*-Butyl Acrylate^a

entry	base	solvent	<i>T</i> (°C)	yield (%)	TON	TOF ^b
1	K ₂ CO ₃	DMF	145	81	8100	405
2	Na ₂ CO ₃	DMF	145	92	9200	460
3	NaOAc	DMF	145	3	300	15
4	K ₃ PO ₄	DMF	145	78	7800	390
5	DIPEA	DMF	145	5	500	25
6	MDCHA	DMF	145	13	1300	65
7	Na ₂ CO ₃	DMA	145	80	8000	400
8	Na ₂ CO ₃	NMP	145	40	4000	200
9	Na ₂ CO ₃	DMSO	145	9	900	45
10	Na ₂ CO ₃	DMF	130	44	4400	220
11	Na ₂ CO ₃	DMF	145	89 ^c	8900	445
12	Na ₂ CO ₃	DMF	145	12 ^d	1200	60
13	Na ₂ CO ₃	DMF	145	22 ^e	2200	110
14	Na ₂ CO ₃	DMF	145	51 ^f	5100	255

^a Reaction conditions: bromoanisole (1 mmol), *n*-butyl acrylate (2 mmol), base (1.2 mmol), solvent (2 mL) for 20 h. ^b TOF = turnover frequency (mol product per mol catalyst h⁻¹). ^c **4b** was used. DIPEA = *N,N*-diisopropylethylamine; MDCHA = *N*-methyl-dicyclohexylamine. ^d With Pd(OAc)₂. ^e With picolinic acid/Pd(OAc)₂ (1:1). ^f With picolinic acid/Pd(OAc)₂ (2:1).

by TGA (see Supporting Information). It was therefore of interest to examine the activity of the **4a** and **4b** complexes as catalysts for Heck and Suzuki coupling reactions.

To begin our study, we examined the Heck reaction between aryl halides and olefins, and the results are presented in Tables 1 and 2. In order to optimize the efficiency of the catalytic system, we initially examined the coupling of bromoanisole and *n*-butyl acrylate in the presence of **4a** under a variety of reaction conditions, and the progress of the reaction was monitored by gas chromatography. Among the bases employed, Na₂CO₃ was found to be the best in the present protocol (Table 1, entry 2). Excellent yield of 4-methoxy-*trans*-cinnamic acid *n*-butyl ester was isolated in 92% yield by carrying out the reaction in *N,N*-dimethylformamide (DMF) at 145 °C for 20 h. It was found that in the absence of ligand, Pd(OAc)₂ indeed could catalyze the Heck reaction,²¹ but the maximum yield was 12% in our

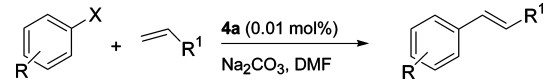
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TABLE 2. Heck Reaction of Aryl Halides and Olefins^a


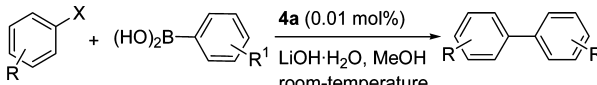
entry	R, X	R ¹	yield (%)	TON	TOF
1	H, Br	Ph	94	9400	470
2	H, Br	CO ₂ Bu ⁿ	92	9200	460
3	H, Br	4-Me-C ₆ H ₄	93	9300	465
4	4-MeOC, Br	Ph	91	9100	455
5	4-MeOC, Br	CO ₂ Bu ⁿ	45	4500	225
6	4-NO ₂ , Br	Ph	92	9200	460
7	4-NO ₂ , Br	CO ₂ Bu ⁿ	90	9000	450
8	4-Me, Br	Ph	95	9500	475
9	4-Me, Br	CO ₂ Bu ⁿ	93	9300	465
10	4-Me, Br	4-Me-C ₆ H ₄	92	9200	460
11	4-MeO, Br	Ph	94	9400	470
12	4-MeO, Br	CO ₂ Bu ⁿ	92	9200	460
13	4-MeO, Br	4-Me-C ₆ H ₄	90	9000	450
14	H, I	Ph	95	9500	475
15	H, I	CO ₂ Bu ⁿ	96	9600	480
16	H, I	4-Me-C ₆ H ₄	90	9000	450
17	4-Me, I	Ph	94	9400	470
18	4-Me, I	CO ₂ Bu ⁿ	95	9500	475
19	4-Me, I	4-Me-C ₆ H ₄	91	9100	455
20	4-MeO, I	Ph	94	9400	470
21	4-MeO, I	CO ₂ Bu ⁿ	90	9000	450
22	4-MeO, I	4-Me-C ₆ H ₄	88	8800	440
23	4-NO ₂ , Cl	Ph	70 ^b	70	3.5
24	4-NO ₂ , Cl	4-Me-C ₆ H ₄	80 ^b	80	4.0

^a Reaction conditions: aryl halide (1 mmol), olefin (2 mmol), Na₂CO₃ (1.2 mmol), DMF (2 mL) at 145 °C for 20 h. ^b With 1 mol % **4a** at 160 °C.

reaction conditions (entry 12) (compared to 9% as reported by Yao et al.^{19a} with 0.1 mol % Pd(OAc)₂). The same reaction was performed using picolinic acid/Pd(OAc)₂ in different Pd:ligand ratios, and the yields obtained were lower than for the catalyst **4a** (entries 13 and 14). The strength of the Pd-amidate bond, chelation, or steric shielding of the metal center have greater effect on the catalytic activity. No marked difference in the reactivity between **4a** and **4b** was observed (entries 2 vs 11).

To explore the scope of the reactions catalyzed by **4a**, we next examined the application of **4a** to the cross-coupling of aryl halides with olefins under our optimized conditions (0.01 mol % **4a**, 1.2 equiv of Na₂CO₃, DMF, 145 °C), and the results are presented in Table 2. It is clear from the Table 2 that aryl bromides containing electron-withdrawing and electron-donating groups are coupled in high yields, with turnover numbers of about 10⁴ (entries 4–13). Besides aryl bromides, aryl iodides could also be successfully used under the same reaction conditions (entries 14–22). Moreover, the catalysts were stable and active enough to handle electron-deficient aryl chlorides at 160 °C (entries 23 and 24).

We next explored the efficacy of **4a** in the Suzuki reactions. It was found that **4a** was active enough to promote the Suzuki reaction at room temperature in the presence of air. After extensive screening, the following set of standard reaction conditions were established with respect to the aryl halide: 0.01 mol % **4a**, 1.5 equiv of ArB(OH)₂, and 1.2 equiv of LiOH·H₂O in methanol (see Supporting Information, Table S1). Here also we observed no marked difference in the reactivity between **4a** and **4b** (Table 3, entries 3 vs 4). A variety of aryl halides and boronic acids were subjected to the optimized conditions mentioned above, and the results are shown in Table 3. The room-temperature Suzuki reaction worked well with both

TABLE 3. Suzuki Reaction of Aryl Halides and Arylboronic Acids^a


entry	R, X	R ¹	time(h)	yield (%)	TON	TOF
1	H, Br	H	5	84	8400	1680
2	4-Me, Br	H	10	76	7600	760
3	4-MeO, Br	H	10	75	7500	750
4	4-MeO, Br	H	10	70 ^b	7000	700
5	4-MeOC, Br	H	5	95	9500	1900
6	4-NO ₂ , Br	H	5	94	9400	1880
7	2-MeO, Br	H	10	45	4500	450
8	H, Br	4-MeO	10	55	5500	550
9	H, Br	4-Me	10	76	7600	760
10	H, Br	2-Me	10	80	8000	800
11	H, Br	3-Me	10	74	7400	740
12	4-Me, Br	4-MeO	16	81 ^c	8100	506
13	4-MeO, Br	4-MeO	16	78 ^c	7800	488
14	4-MeOC, Br	4-MeO	16	85 ^c	8500	531
15	H, I	H	5	96	9600	1920
16	4-Me, I	H	5	93	9300	1860
17	4-MeO, I	H	5	94	9400	1880
18	H, I	4-MeO	5	82	8200	1640
19	H, I	4-Me	5	84	8400	1680
20	H, I	2-Me	5	85	8500	1700
21	H, I	3-Me	5	84	8400	1680
22	4-Me, I	4-MeO	5	85	8500	1700
23	4-MeO, I	4-MeO	5	82	8200	1640
24	4-MeO, Br	H	10	61 ^e	6100	610

^a Reaction conditions: aryl halide (1 mmol), arylboronic acid (1.5 mmol), LiOH·H₂O (1.2 mmol), and methanol (2 mL). ^b **4b** was used. ^c Reaction carried out at 50 °C. ^e With Pd(OAc)₂.

electron-rich and electron-poor aryl bromides, and the turnover numbers were about 10⁴ (entries 2–6). The sterically hindered *ortho*-substituted substrates could also couple efficiently at room temperature with low catalyst loading (entries 7 and 10). The reactions corresponding to entries 12–14 were performed at 50 °C in order to give good isolated yields. Aryl iodides could also be successfully used under the same reaction conditions (entries 15–23). The resulting products were consistently obtained in moderate to good isolated yields. It is very clear from results that both trifunctional palladium complexes **4a** and **4b** are stable enough and active for the Heck and Suzuki coupling reactions.

The important advantages associated with these catalysts, compared to many of the previous phosphine-free catalysts, are that these catalysts are air- and heat-stable and have long lifetimes. We have achieved room-temperature Suzuki reactions, which were accomplished previously either by using complicated phosphine or heterocyclic carbene ligands²² or by using a relatively high loading of Pd (i.e., >1 mol %).²³ Unlike most previously reported systems for C–C cross-coupling reactions, additional co-catalysts such as [NBu₄]Br or [PPh₄]Cl are not required to achieve high catalytic activity.²⁴ Moreover, we have

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achieved high turnover numbers with different aryl bromides in both Heck and Suzuki reactions.

In conclusion, we have shown that the trifunctional *N,N,O*-tridentate palladium(II) complexes **4a** and **4b** are excellent catalysts for Heck and room-temperature Suzuki reactions. It is also shown that the amidate donor-functional group was a good supporting functionality to enhance the thermal stability and at the same time enhance the activity of the Pd catalysts in C–C cross-coupling reactions. We have also demonstrated the importance of multifunctional ligands for Pd catalysis.

Experimental Section

Synthesis of Complex 4a. Compounds **3a** and **3b** were prepared according to our previously reported work. The *N,N,O*-tridentate ligand **3a** (266.4 mg, 1.2 mmol) was added to a stirred orange-colored suspension of palladium acetate (224.49 mg, 1 mmol) in tetrahydrofuran (20 mL) in one portion. After the solution stirred for 12 h at room temperature, a pale yellow precipitate was obtained. The solvent was removed completely under reduced pressure, and the resulting solid was washed with excess diethylether to obtain pure **4a** in 94% yield. Compound **4b** was prepared following the same experimental procedure using **3b** as tridentate ligand. Complex **4a**: Mp, decomposed to black metal above 262 °C; ¹H NMR (200 MHz, CDCl₃, TMS) δ 1.20–1.23 (m, 6H), 2.61–2.71 (m, 1H), 4.32 (d, *J* = 3.8 Hz, 1H, CH), 7.45–7.50 (m, 1H), 7.76 (d, *J* = 6.8 Hz, 1H), 8.01 (dt, *J* = 1.3, 7.7 Hz, 1H), 8.23 (d, *J* = 5.5 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 18.1, 19.7, 31.6, 69.1, 125.1, 126.8, 140.1, 146.4, 156.3, 168.0, 191.9; IR (KBr) $\bar{\nu}$ = 1737, 1637 cm⁻¹ (C=O), 1600, 1560 cm⁻¹ (C=C), 1240 cm⁻¹ (C–O), 1099 cm⁻¹ (C–N); ESI-MS (*M* + *H*)⁺ = 327, (*M* + *Na*)⁺ = 349; HRMS calcd for C₁₁H₁₂N₂O₃NaPd (*M* + *Na*)⁺ = 348.9780, found 348.9798. Anal. Calcd for C₁₁H₁₂N₂O₃Pd: C 40.45, H 3.70, N 8.58. Found: C 40.27, H 3.69, N 8.43. Complex **4b**: Mp, decomposed to black metal above 282 °C; ¹H NMR (200 MHz, DMSO-*d*₆, TMS) δ 2.98 (dd, *J* = 2.9, 13.2 Hz, 1H), 3.49 (dd, *J* = 5.9, 13.16 Hz, 1H), 4.31–4.44 (m, 1H, CH), 7.08–7.29 (m, 6H), 7.68 (t, *J* = 7.3, 13.2 Hz, 1H), 7.78 (d, *J* = 7.3 Hz, 1H), 8.23 (t, *J* = 7.3, 15.4 Hz, 1H); ¹³C NMR (50 MHz, DMSO-*d*₆) δ 37.0, 63.5, 124.9, 126.2, 127.8, 128.1, 129.6, 137.6, 141.5, 148.0, 155.0, 167.3, 183.5; IR (KBr) $\bar{\nu}$ = 1734, 1636 cm⁻¹ (C=O), 1563 cm⁻¹ (C=C), 1239 cm⁻¹ (C–O), 1101 cm⁻¹ (C–N); ESI-MS (*M* + *H*)⁺ = 375, (*M* + *Na*)⁺ = 397; HRMS calcd for C₁₅H₁₃N₂O₃ Pd (*M* + *H*)⁺ 374.9960, found

374.9962. Anal. calcd for C₁₅H₁₂N₂O₃Pd: C 48.08, H 3.23, N 7.48. Found: C 47.64, H 3.14, N 7.34.

Typical Procedure for the Heck Reaction. The reaction vessel was charged with bromobenzene (1 mmol), *n*-butyl acrylate (2 mmol), Na₂CO₃ (1.2 mmol), and the catalyst (0.01 mol %) in *N,N*-dimethylformamide (2 mL). The reaction mixture was heated to 145 °C, and the progress of reaction was monitored by GC. At the end of the reaction, the reaction mixture was cooled to room temperature, diluted with EtOAc (20 mL), and washed with 1 N aq HCl and water. The combined organic phase was dried over anhydrous Na₂SO₄. After removal of the solvent, the residue was subjected to column chromatography on silica gel using ethyl acetate and hexane mixtures to afford the Heck product in high purity. *trans*-Cinnamic acid *n*-butyl ester: ¹H NMR (300 MHz, CDCl₃, TMS) δ 0.97 (t, *J* = 7.6 Hz, 3H), 1.37–1.50 (m, 2H), 1.63–1.72 (m, 2H), 4.18 (t, *J* = 6.8 Hz, 2H), 6.39 (d, *J* = 15.9 Hz, 1H), 7.33–7.34 (m, 3H), 7.48–7.50 (m, 2H), 7.63 (d, *J* = 15.9 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 13.6, 19.0, 30.7, 63.8, 118.2, 127.8, 128.5, 129.7, 134.4, 144.0, 166.0.

Typical Procedure for the Suzuki Reaction. The reaction vessel was charged with bromobenzene (1 mmol), phenylboronic acid (1.5 mmol), lithium hydroxide monohydrate (1.2 mmol), and the catalyst (0.01 mol %) in methanol (2 mL). The reaction mixture was stirred at the given temperature, and the progress of reaction was monitored by GC. At the end of the reaction, the methanol was removed under reduced pressure, and the reaction mixture was diluted with EtOAc (20 mL) and washed with 1 N aq HCl and water. The combined organic phase was dried over anhydrous Na₂SO₄. After removal of the solvent, the residue was subjected to column chromatography on silica gel using ethyl acetate and hexane mixtures to afford the Suzuki product in high purity. Biphenyl: ¹H NMR (300 MHz, CDCl₃, TMS) δ 7.28–7.33 (m, 2H), 7.40 (t, *J* = 7.6 Hz, 4H), 7.56 (d, *J* = 8.3 Hz, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 127.12, 127.20, 128.7, 141.2.

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Supporting Information Available: General experimental procedures, characterization data of complexes and products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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