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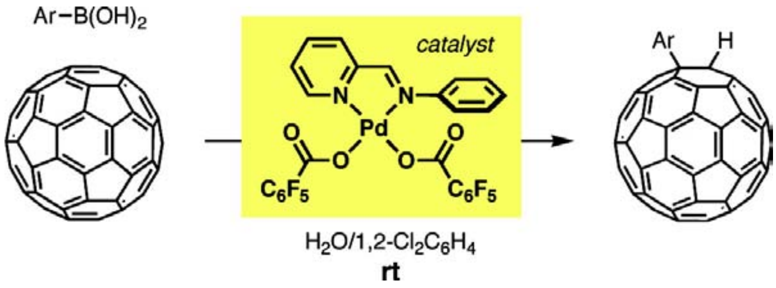

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A Bench-Stable Pd Catalyst for the Hydroarylation of Fullerene with Boronic Acids

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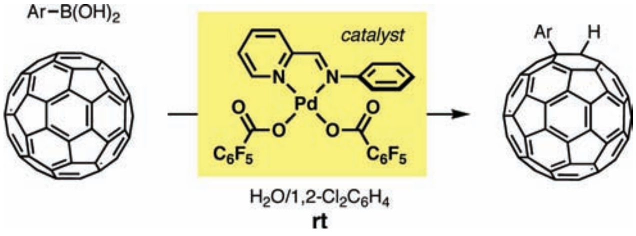
ABSTRACT



A Pd(II) catalyst for the hydroarylation of fullerene with boronic acids is presented. Treatment of C_{60} with an arylboronic acid in the presence of a catalytic amount of Pd(2-PyCH=NPh)($OCOC_6F_5$)$_2$ in H_2O/1,2-$Cl_2C_6H_4$ at room temperature furnishes the hydroarylation product (Ar−C_{60}−H) in good yield with high selectivity. This complex possesses high catalytic activity paired with bench stability in the solid state.

The chemical modification of fullerenes provides an important opportunity for tailoring the properties of nanocarbon-based materials.[1] Although a number of privileged reactions have emerged,[1] the synthetic toolbox of highly versatile reactions for fullerene functionalization remains comparatively limited. Thus, the development of new general synthetic methods is critical for the synthesis of new nanocarbon-based materials.

Recently, we initiated a program aimed at the development of new functionalization chemistry of nanocarbons using transition metal catalysts.[2,3] As our initial foray into the area of nanocarbon chemistry, we developed a Rh-catalyzed hydroarylation of C_{60} with organoboron reagents

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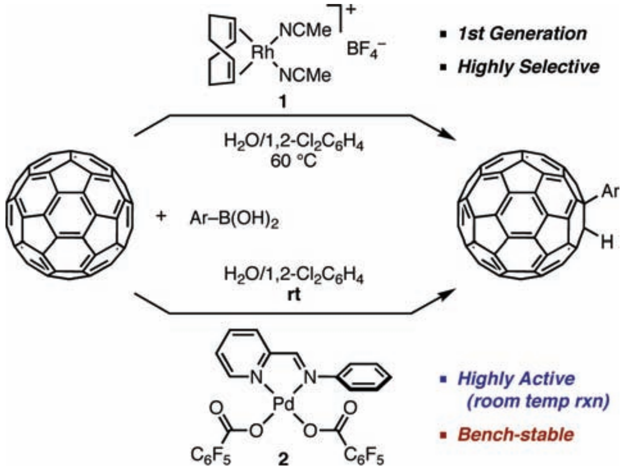
(Scheme 1).[2,4] Under the influence of catalytic amounts of $[Rh(cod)(CH_3CN)_2]BF_4$ (**1**), arylboronic acids react with C_{60} in the presence of water to give a formal hydroarylation product ($Ar-C_{60}-H$).[2] This reaction enables the introduction of various aryl groups and a hydrogen atom on the fullerene surface. This catalytic reaction has been developed on the basis of the ability of Rh(I) complexes to catalyze the hydroarylation of electron-deficient alkenes and alkynes with arylboronic acids,[5] and of the general behavior of C_{60} as an electron acceptor.[1,6]

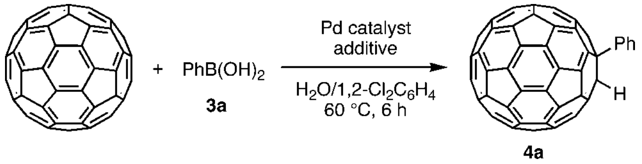
Scheme 1. Hydroarylation of Fullerene with Boronic Acids Catalyzed by Rh Complex **1** and Pd Complex **2**



Inspired by the parallel progress of Pd(II) catalysis in organoboron-based hydroarylation chemistry,[7−13] we decided to investigate the use of Pd(II) complexes as potential second-generation catalysts for the functionalization of C_{60}. Herein we report a highly active yet bench-stable Pd(II) catalyst (**2**) for the hydroarylation of C_{60} with boronic acids (Scheme 1).

In early experiments, we found that a cationic Pd(II) complex such as $[Pd(dppe)(PhCN)_2]SbF_6$ (Miyaura catalyst)[9] can catalyze the reaction between C_{60} and $PhB(OH)_2$ (**3a**) in H_2O/1,2-$Cl_2C_6H_4$, furnishing the corresponding hydrophenylation product **4a** (Table 1, entries 1 and 2). As in the rhodium-catalyzed reaction,[2] the addition takes place across the C═C bond between the two six-membered rings on C_{60} (1,2-bond). Although $Pd(OAc)_2$ alone is nearly inactive (entry 3), the addition of 2,2′-bipyridyl (bpy)[10] as a ligand (Lu catalyst) affords **4a** in 17% yield (entry 4). Catalytic activity is further increased with CF_3CO_2H (20 mol %) as additive, producing **4a** in 40% yield (entry 5).

Table 1. Discovery of Palladium Catalysis for the Hydroarylation of C_{60} with Boronic Acids[a]



entry	Pd catalyst	additive (amount)	yield (%)[b]
1[c]	$PdCl_2(dppe)$[d]	$AgSbF_6$ (20%)	16
2[e]	$[Pd(dppe)(PhCN)_2](SbF_6)_2$		40
3	$Pd(OAc)_2$		3
4	$Pd(OAc)_2$/bpy[f]		17
5	$Pd(OAc)_2$/bpy[f]	CF_3CO_2H (20%)	40

[a] Reaction conditions: C_{60} (60 μmol), **3a** (90 μmol), Pd catalyst (10 mol %), 1,2-$Cl_2C_6H_4$ (7.2 mL), H_2O (0.6 mL), 60 °C, 6 h. [b] Determined by HPLC analysis with C_{70} as an internal standard. [c] Reaction was conducted for 12 h. [d] dppe: 1,2-bis(diphenylphosphino)ethane. [e] Reaction was conducted at 23 °C. [f] bpy: 2,2′-bipyridyl. 20 mol % of bpy was employed.

On the basis of these encouraging results, further optimization of catalyst was conducted. Following the $Pd(OAc)_2$/bpy/CF_3CO_2H catalyst lead (Table 1, entry 5),

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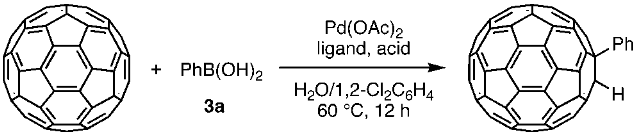
(14) In view of cost, simplicity, and stability, the catalyst modification of $[Pd(dppe)(PhCN)_2]SbF_6$ was not conducted.

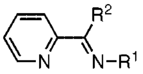
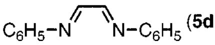
(15) Throughout this paper, "selectivity" stands for a ratio of the quantity of desired product (**4**) over the quantity of substrate (C_{60}) converted (Orchin, M.; Macomber, R. S.; Pinhas, A. R.; Wilson, R. M. *The Vocabulary and Concepts of Organic Chemistry*, ed.; Wiley-Interscience: Hoboken, NJ, 2005). The most common side products for reactions where the selectivity is low are multiple hydroarylation products.

various nitrogen-based ligands and acids were screened (Table 2, molar ratio, C_{60}/**3a**/$Pd(OAc)_2$/ligand/acid = 1.0:1.5:0.1:0.2:0.2).[14] The yield and selectivity[15] were determined by HPLC analysis of the crude reaction mixture with C_{70} as an internal standard.

Table 2. Optimization of Palladium Catalyst for the Hydroarylation of C_{60} with Boronic Acids[a,b]



4a

entry	ligand	acid	yield[b]	selec[b,c]
1	2,2'-bipyridyl (bpy)	CH_3CO_2H	29%	83%
2	bpy	CCl_3CO_2H	40%	80%
3	bpy	CF_3CO_2H	52%	90%
4	bpy	$C_6F_5CO_2H$	48%	>95%
5[d]	pyridine	$C_6F_5CO_2H$	3%	nd[e]
				
6	$R^1 = C_6H_5$, R^2 = H (**5a**)	$C_6F_5CO_2H$	61%	>95%
7	$R^1 = C_6H_5$, $R^2 = CH_3$ (**5b**)	$C_6F_5CO_2H$	25%	83%
8	$R^1 = {}^cC_6H_{11}$, R^2 = H (**5c**)	$C_6F_5CO_2H$	15%	83%
9	 (**5d**)	$C_6F_5CO_2H$	2%	nd[e]

[a] Reaction conditions: C_{60} (60 μmol), **3a** (90 μmol), $Pd(OAc)_2$ (10 mol %), ligand (20 mol %), acid (20 mol %), 1,2-$Cl_2C_6H_4$ (7.2 mL), H_2O (0.9 mL), 60 °C, 12 h, under argon. [b] Determined by HPLC analysis with C_{70} as an internal standard. [c] Selectivity: [yield of **4a**]/[conversion of C_{60}]. [d] 40 mol % of pyridine was employed. [e] Not determined.

First, the effect of acid was examined in combination with $Pd(OAc)_2$/bpy (entries 1−4). By increacing the acidity of the carboxylic acid additive (CH_3CO_2H → CCl_3CO_2H → CF_3CO_2H), an increase in product yield and selectivity was observed. Interestingly, the use of $C_6F_5CO_2H$ resulted in highest selectivity for **4a** (>95%) among those acids screened, albeit with moderate product yield (entry 4). Next we examined various nitrogen-based ligands in combination with $Pd(OAc)_2$/$C_6F_5CO_2H$ (entries 5−9). Since the use of pyridine in place of bpy shut down the reaction (entry 5), the use of a nitrogen-based bidentate ligand seems to be important for activity and/or stability of the Pd catalyst. After extensive screening of such ligands, 2-PyCH═NPh (**5a**) was identified as an optimal ligand, producing **4a** in 61% yield with very high selectivity (>95%) (entry 6). Although the reason is not clear yet, **5a** is a far superior ligand among other related imine-based ligands such as 2-PyC(CH_3)═NPh (**5b**), 2-PyCH═N(*cyclo*-C_6H_{11}) (**5c**), and PhN═CH−CH═NPh (**5d**) (entries 7−9).

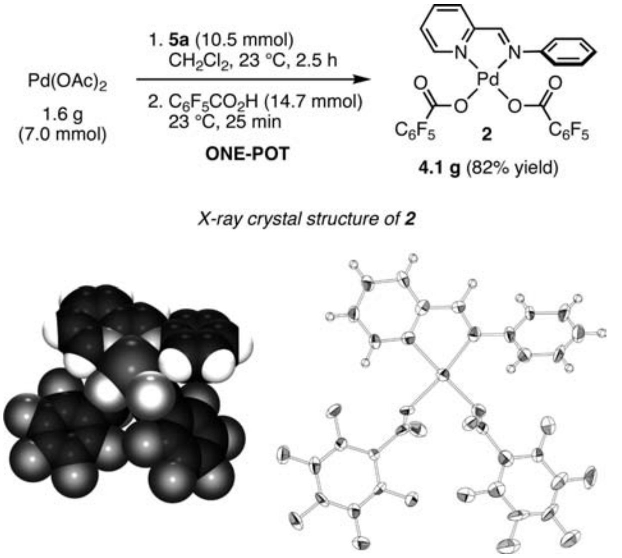
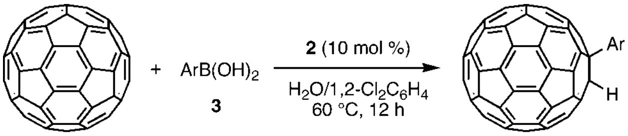
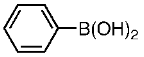
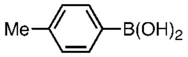
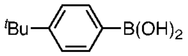
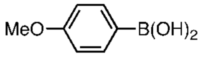
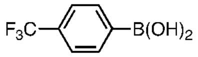
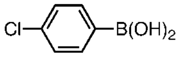
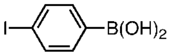
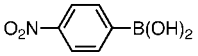
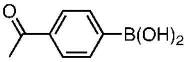
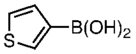


Figure 1. Gram-scale synthesis and X-ray crystal structure of **2**.

Table 3. Hydroarylation of C_{60} with Boronic Acids Catalyzed by Palladium Complex **2**[a]



4

entry	ArB(OH)$_2$ (**3**)		yield of **4** (%)[b]
1		**3a**	59 (54)
2		**3b**	51 (49)
3		**3c**	60 (51)
4		**3d**	57 (45)
5		**3e**	52 (45)
6		**3f**	51 (45)
7		**3g**	50 (46)
8		**3h**	31 (22)
9		**3i**	29 (21)
10		**3j**	35 (27)

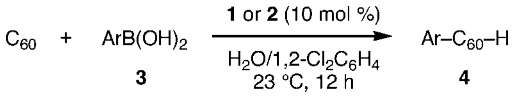
[a] Reaction conditions: C_{60} (60 μmol), $ArB(OH)_2$ (**3**: 90 μmol), **2** (6.0 μmol), 1,2-$Cl_2C_6H_4$ (7.2 mL), H_2O (0.6 mL), 60 °C, 12 h, under argon. [b] Yield of **4** determined by HPLC analysis with C_{70} as an internal standard. The number in parentheses is the isolated yield.

With this interesting new catalytic system in hand, we then attempted to isolate the Pd species generated in situ from $Pd(OAc)_2$/**5a**/$C_6F_5CO_2H$ (Figure 1). By treating $Pd(OAc)_2$ with **5a** and $C_6F_5CO_2H$ in sequence, the complex Pd(2-PyCH═NPh)$(OCOC_6F_5)_2$ (**2**) can be isolated as an air-stable yellow solid.[16] The routine gram-scale preparation of **2** can be performed by a similar procedure (4.1 g, 82%). The X-ray crystal structure reveals a typical square-planar coordination around the Pd(II) center (Figure 1). A notable feature of **2** is its shelf stability in the solid state. Virtually no decomposition of **2** has been detected by NMR after prolonged exposure (>6 months) to air and moisture. Since the corresponding palladium diacetate complex easily decomposes under air/moisture, the pentafluorobenzoate moiety clearly enhances not only the activity but also the stability of palladium catalyst.

The thus-isolated Pd complex **2** can catalyze the reaction of C_{60} with various electronically diverse arylboronic acids (**3a**−**j**) in H_2O/1,2-$Cl_2C_6H_4$ (Table 3). Interestingly, unlike the previous Rh-catalyzed reaction,[2] electron-deficient aryl groups can be introduced onto C_{60} with reasonable efficiency. This permits the incorporation of functionality, such as acetyl group, nitro group, and halogens, onto C_{60}. In particular, tolerance to carbon−halogen bonds is attractive for further synthetic manipulations. In all cases examined thus far, the monoadditon product (**4**) was obtained with high selectivities (>90%), as judged by the HPLC analysis of crude reaction mixture.

More interestingly, room temperature hydroarylation is possible with Pd catalyst **2** (Table 4). In all cases examined, the hydroarylation products (**4**) were produced with reasonable efficiency. It should be noted that under otherwise identical conditions, our first-generation Rh catalyst **1** is virtually inactive for room temperature hydroarylation (Table 4). More interestingly, the reaction proceeds under air with similar efficiency (entry 2).

Table 4. Room-Temperature Hydroarylation of C_{60}[a]



entry	3	yield of 4[b] (%)	
		Rh catalyst **1**	Pd catalyst **2**
1	**3a**	<1	49
2	**3a**	<1	49[c]
3	**3b**	<1	47
4	**3c**	<1	41
5	**3d**	5	42
6	**3e**	<1	38
7	**3f**	<1	51

[a] Reaction conditions: C_{60} (60 μmol), $ArB(OH)_2$ (**3**: 90 μmol), catalyst (6.0 μmol), 1,2-$Cl_2C_6H_4$ (7.2 mL), H_2O (0.6 mL), 23 °C, 12 h, under argon. [b] Yield of **4** determined by HPLC analysis with C_{70} as an internal standard. [c] Reaction was conducted under air.

In summary, a new Pd(II) catalyst for the hydroarylation of fullerene with boronic acids has been developed. The complex Pd(2-PyCH═NPh)$(OCOC_6F_5)_2$ (**2**) possesses good catalytic activity paired with bench stability in the solid state. In addition to significantly broadening the scope of fullerene functionalization chemistry, the Pd(II) catalyst **2** may demonstrate utility in small-molecule reactions.[17]

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Supporting Information Available: Experimental procedures and characterization data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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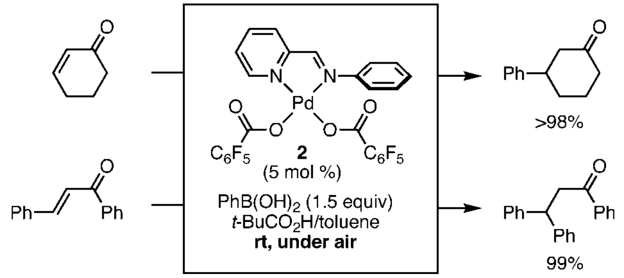
(16) Similar Pd(II) complexes have been reported for the bis-alkoxycarbonylation of styrene: Bianchini, C.; Lee, H. M.; Mantovani, G.; Meli, A.; Oberhauser, W. *New J. Chem.* **2002**, *26*, 387.

(17) For example, we have identified that the Pd catalyst **2** is active in the hydroarylation (conjugate addition) of cyclic and acyclic enones with boronic acids. The reactions proceed at room temperature under air (see the Supporting Information for details):



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