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Synthesis of [60]Fulleroindolines: Palladium-Catalyzed Heteroannulations of [60]Fullerene with *o*-Iodoanilines

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The palladium-catalyzed reaction of C_{60} with a variety of *o*-iodoanilines afforded the first synthesis of C_{60}-fused indoline derivatives. A plausible reaction mechanism was proposed.

Fullerene chemistry has been extensively studied over the years.[1] Various methodologies have been explored to functionalize fullerenes. For example, C_{60}-fused pyrrolines have been synthesized by several different approaches, such as through the reaction of C_{60} with nitrile ylides,[2,3] with a cyclic azomethine ylide,[4] with isocyanides,[5] with *N*-(diphenylmethylene)glycinate esters,[6] with sulfide-bearing imines of glycine esters,[7] and with benzylamine imines.[8] Despite a plethora of fullerene derivatives being synthesized, there is still a strong demand to develop more and better protocols to prepare fullerene compounds with desired and yet-unknown specific structures because of their potential applications in material[9] and biomedical sciences.[10] Recently, our group[11] accomplished the first C_{60}-fused pyrroline derivatives, of which a nitrogen atom directly attached to the fullerene skeleton, through $Mn(OAc)_3$-mediated radical reaction of C_{60} with β-enamino carbonyl compounds. However, this method is ineffective for the synthesis of C_{60}-fused indoline derivatives, the analogues of the corresponding pyrroline derivatives.

Although a large variety of chemical reactions have been exploited to derivatize fullerenes,[1] transition metal salt-mediated reactions of fullerenes are much less investigated.[5,12−21] Fur-

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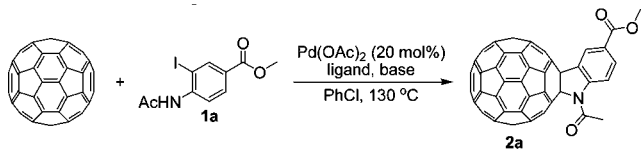
TABLE 1. Screening of the Reaction Conditions[a]



entry	ligand (mol %)	base (equiv)	yield (%)[b]
1	PPh_3 (20)	no	20 (77)
2	PPh_3 (20)	DMAP (2)	25 (86)
3	LiCl (100)	DMAP (2)	23 (74)
4[c]	PPh_3 (20)	Cs_2CO_3 (2)	32 (80)
5	PPh_3 (20)	DABCO·$6H_2O$ (2)	36 (95)
6	DPPE (10)	DABCO·$6H_2O$ (2)	41 (95)
7	DPPE (10)	Cs_2CO_3 (2)	31 (70)

[a] Unless otherwise specified, all the reactions were performed with 0.050 mmol of C_{60}, 0.10 mmol of **1a**, 0.010 mmol of $Pd(OAc)_2$, ligand, and base in chlorobenzene (8 mL) at 130 °C for 24 h. [b] Isolated yield. Values in parentheses were based on consumed C_{60}. [c] Conducted for 5 h.

thermore, few examples of them employed palladium complexes in fullerene chemistry,[13] although palladium chemistry has been widely applied in numerous fields of organic chemistry. Luh's group reported the first example, that is, the [2+3] cycloaddition of C_{60} with $CH_2{=}C(CH_2OAc)CH_2SiMe_3$, in which a stoichiometric amount of $Pd(PPh_3)_4$ was required.[13a] Subsequently, the same group studied the [2+3] cycloaddition reaction between C_{60} and *cis*-$HOCH_2CH{=}CHCH_2OCO_2Et$ utilizing 10−50 mol % of $Pd(PPh_3)_4$ and 1 equiv of 1,2-bis(diphenylphosphino)ethane (DPPE).[13b] Murata's group described the reaction of C_{60} with preformed palladacyclopentadiene complexes affording cyclohexadiene-type adducts.[13c] Recently, Itami's group successfully realized the hydroarylation of C_{60} with boronic acids catalyzed by $Pd(2\text{-}PyCH{=}NPh)(OCOC_6F_5)_2$,[13d] and Pd-catalyzed C−H bond transformations of organo(hydro)fullerenes.[13e] On the other hand, over the past decades, Larock's group has developed a series of Pd-catalyzed heteroannulations of *o*-iodoanilines with a broad scope of partners for the synthesis of a wide variety of nitrogen-containing heterocycles.[22] To the best of our knowledge, however, this strategy has not been applied to the functionalization of C_{60} yet. In continuation of our interest in developing metal salt-promoted reactions of C_{60},[16a,17c,f,20] herein we report the first Pd-catalyzed heteroannulations of C_{60} with various *o*-iodoaniline derivatives to give C_{60}-fused indoline derivatives.

In our preliminary experiments, we found that methyl 4-acetylamino-3-iodobenzoate (**1a**) possessed low reactivity, so we chose **1a** as the model substrate to screen the reaction conditions (Table 1). At the onset, when a mixture of C_{60} (0.05 mmol) and **1a** (2 equiv) was treated with $Pd(OAc)_2$ (20 mol %) and PPh_3 (20 mol %) in chlorobenzene (8 mL) at 130 °C for 24 h, the desired C_{60}-fused indoline derivative **2a** was obtained in 20% yield along with 74% of recovered C_{60} (Table 1, entry 1). However, the conversion efficiency and product yield needed to be further improved. The further addition of 2 equiv of 4-*N*,*N*-dimethylaminopyridine (DMAP) as the base resulted in somewhat higher yield (25%) and cleaner reaction (entry 2). However, the addition of 1 equiv of LiCl as the ligand, in place of PPh_3, had little beneficial effect (entry 3). The combination of 20 mol % of PPh_3 as the ligand and 2 equiv of 1,4-diazabicyclo[2,2,2]octane·$6H_2O$ (DABCO·$6H_2O$) as the base

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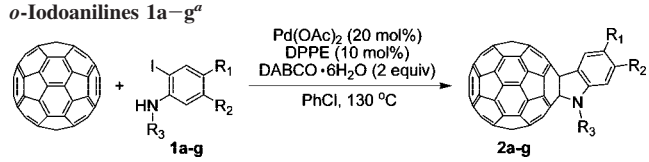
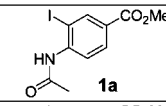
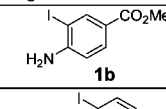
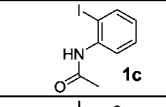
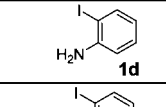
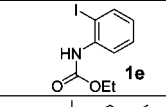
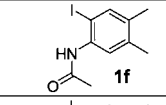
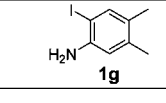
TABLE 2. Results for the Pd-Catalyzed Reaction of C_{60} with *o*-Iodoanilines 1a−g[a]



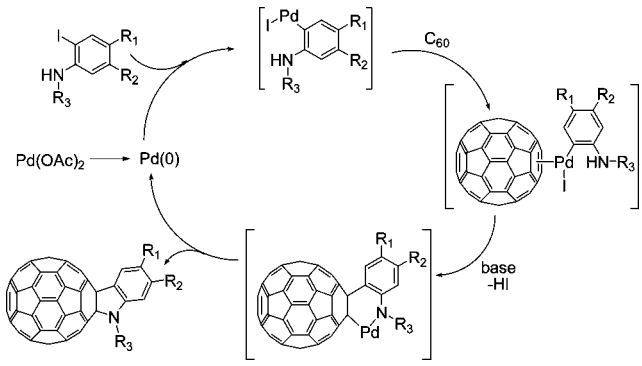
entry	substrate	product	yield (%)[b]
1	 **1a**	**2a**	41 (95)
2	 **1b**	**2b**	33 (94)
3	 **1c**	**2c**	40 (83)
4	 **1d**	**2d**	30 (91)
5	 **1e**	**2e**	31 (91)
6	 **1f**	**2f**	42 (84)
7	 **1g**	**2g**	31 (86)

[a] All the reactions were performed with 0.050 mmol of C_{60}, 0.10 mmol of **1**, 0.010 mmol of $Pd(OAc)_2$, 0.0050 mmol of DPPE, and 0.10 mmol of DABCO·$6H_2O$ in chlorobenzene (8 mL) at 130 °C for 24 h. [b] Isolated yield. Values in parentheses were based on consumed C_{60}.

under otherwise identical conditions gave significantly improved yield of product **2a** (36%, entry 5). Replacing PPh_3 with 10 mol % of DPPE as the ligand resulted in a further increase of the product yield (41%, entry 6). However, the combination of 10 mol % of DPPE as the ligand and 2 equiv of Cs_2CO_3 as the base afforded only 31% yield of product **2a** (Table 1, entry 7).

With the optimal conditions in hand, the scope of this annulation was explored by using a variety of substrates as illustrated in Table 2. We were pleased to find that all of the examined *o*-iodoanilines with a substituent on the phenyl ring or on the nitrogen atom were well tolerated, and they all gave good yields of the desired C_{60}-fused indoline derivatives **2a**−**g**, ranging from 30% to 42% (83−95% based on consumed C_{60}). Generally, *o*-iodoaniline derivatives with the acetyl group on the nitrogen atom were superior substrates to those without the carbonyl group, which gave less conversion of C_{60} and afforded lower yields (Table 2, entry 1 vs. 2, entry 3 vs. 4, entry 6 vs. 7). The resulting palladium species from **1a**, **1c**, or **1f** may be more stable due to the coordination of the carbonyl group to the palladium atom, thus explaining the observed phenomenon. However, the substituents on the phenyl ring of *o*-iodoaniline derivatives had no pronounced effect. Interestingly, substrate **1e** with the COOEt group on the nitrogen atom was less reactive than **1c** with the acetyl group on the nitrogen atom (Table 2, entry 5 vs. 3). Unfortunately, *o*-bromoaniline derivatives such as *N*-(2-bromophenyl)acetamide could not react with C_{60} under the same conditions.

SCHEME 1. Proposed Reaction Mechanism



The structures of C_{60}-fused indoline derivatives **2a**−**g** were fully established by their HRMS, ^{1}H NMR, ^{13}C NMR, FT-IR, and UV−vis spectral data except for the absence of the ^{13}C NMR data of **2c** and **2d** due to their poor solubilities in common organic solvents. Taking **2a** as an example, the MALDI FT-ICR mass spectrum of **2a** gave the correct molecular ion peak at 911.0580. The ^{1}H NMR spectrum of **2a** displayed two singlets at 3.91 and 2.92 ppm for the two methyl groups, and peaks of the three protons on the phenyl ring. In the ^{13}C NMR spectrum of **2a**, there were 26 peaks including two half-intensity ones due to the 58 sp^2-carbons of the C_{60} skeleton in the range of 152−134 ppm and two sp^3-carbons of the C_{60} cage at 87.39 and 70.58 ppm, together with 6 peaks for the aromatic ring, two peaks at 168.49 and 164.67 ppm for the two C═O groups, and two peaks at 51.74 and 27.73 ppm for the two methyl groups, consistent with the C_s symmetry of its molecular structure. The UV−vis spectrum of **2a** showed a peak at 428 nm, which is a characteristic absorption peak for the monoadduct of C_{60} at the [6,6] junction, and is close to that for 1,2-adducts of C_{60} with a nitrogen atom[1j,2b,11] as well as a carbon atom[2,3,12d,15,21] directly attached to the fullerene skeleton. All other indoline-fused C_{60} derivatives (**2b**−**g**) were characterized in the same way.

On the basis of the above reaction results and Larock's previous investigations,[22] a plausible mechanism is shown in Scheme 1. The reaction is assumed to be initiated by the oxidative addition of the aryl iodide to in situ generated Pd(0), followed by coordination of C_{60} to the palladium atom of the resulting arylpalladium intermediate and then insertion into the arylpalladium bond, subsequent nitrogen displacement of the halide in the resulting intermediate to form a six-membered, nitrogen-containing palladacycle, and finally reductive elimination to form the indoline-fused C_{60} derivatives and regenerate Pd(0).

The indoline moiety is a biologically active motif found in alkaloids such as oxaline,[23] neoxaline,[23] mersicarpine,[24] anhydrolycorinone,[25] and oxoassoanine,[26] and pharmaceuticals like 5-hydroxytryptamine receptor antagonists,[27] muscarine receptor agonists and antagonists,[28] or DPP-IV inhibitors,[29] thus giving a hint to potential applications of [60]fulleroindolines in biomedical science.

In conclusion, the Pd-catalyzed annulation of C_{60} with *o*-iodoanilines was realized, and led to the first example of the synthesis of C_{60}-fused indoline derivatives. A possible reaction mechanism was proposed to explain the formation of C_{60}-fused indoline derivatives. Studies on other Pd-catalyzed reactions of C_{60} are currently underway.

Experimental Section

General Procedure for the Preparation of [60]Fulleroindolines 2a−g. To a solution of C_{60} (36.0 mg, 0.050 mmol) in chlorobenzene (8 mL) was sequentially added *o*-iodoaniline derivatives **1** (0.10 mmol), DPPE (2.0 mg, 0.0050 mmol), DABCO·6H$_2$O (22.0 mg, 0.10 mmol), and Pd(OAc)$_2$ (2.2 mg, 0.010 mmol). After being stirred at 130 °C for 24 h, the reaction mixture was filtered through a silica gel plug in order to remove any insoluble material. After evaporation in vacuo, the residue was separated on a silica gel column with carbon disulfide as the eluent to give unreacted C_{60}; subsequent elution with carbon disulfide/dichloromethane afforded fulleroindolines **2**.

2a: ^{1}H NMR (300 MHz, CS$_2$/CDCl$_3$) δ 8.70 (d, J = 1.8 Hz, 1H), 8.24 (dd, J = 8.7, 1.8 Hz, 1H), 7.80 (d, J = 8.7 Hz, 1H), 3.91 (s, 3H), 2.92 (s, 3H); ^{13}C NMR (75 MHz, CS$_2$/CDCl$_3$ with Cr(acac)$_3$ as relaxation reagent) (all 2C unless indicated) δ 168.49 (1C, *C*O), 164.67 (1C, *C*O), 152.16, 147.71, 147.58 (1C), 147.06 (1C), 146.23, 146.21, 146.00, 145.94, 145.68, 145.48, 145.06, 145.05, 144.86, 144.63, 144.50 (1C, aryl *C*), 144.25, 144.21, 143.96, 142.72, 142.57 (6C), 141.90 (6C), 141.51, 141.33, 140.87, 137.34, 136.36, 134.81, 131.62 (1C, aryl *C*), 131.35 (1C, aryl *C*), 127.80 (1C, aryl *C*), 126.21 (1C, aryl *C*), 115.02 (1C, aryl *C*), 87.39 (1C, sp^3-*C* of C_{60}), 70.58 (1C, sp^3-*C* of C_{60}), 51.74 (1C, *C*H$_3$), 27.73 (1C, *C*H$_3$); FT-IR ν/cm^{-1} (KBr) 2946, 2922, 1721, 1683, 1606, 1492, 1433, 1363, 1342, 1302, 1284, 1225, 1196, 1105, 763, 527; UV−vis (CHCl$_3$) λ_{max}/nm (log ε) 257 (5.06), 310 (4.73), 428 (3.59), 684 (2.87); MALDI FT-ICR MS *m*/*z* calcd for $C_{70}H_9NO_3$ [M$^-$] 911.0582, found 911.0580.

2e: ^{1}H NMR (300 MHz, CS$_2$/CDCl$_3$) δ 8.34 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 7.5 Hz, 1H), 7.51 (dd, J = 8.4, 7.5 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 4.48 (q, J = 7.0 Hz, 2H), 1.43 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, CS$_2$/CDCl$_3$ with Cr(acac)$_3$ as relaxation reagent) (all 2C unless indicated) δ 152.50, 152.32 (1C, *C*O), 147.71 (1C), 147.58, 147.11 (1C), 146.26, 146.19, 146.00, 145.89, 145.71, 145.62, 145.05, 144.95, 144.90, 144.77, 144.71, 144.38, 144.21, 142.81, 142.66, 142.62, 142.50, 142.13, 142.05, 141.87, 141.61, 141.60, 140.98 (1C, aryl *C*), 140.87, 137.50, 136.70, 134.78, 129.85 (1C, aryl *C*), 128.55 (1C, aryl *C*), 125.30 (1C, aryl *C*), 124.08 (1C, aryl *C*), 117.78 (1C, aryl *C*), 85.54 (1C, sp^3-*C* of C_{60}), 72.19 (1C, sp^3-*C* of C_{60}), 62.73 (1C, *C*H$_2$), 14.50 (1C, *C*H$_3$); FT-IR ν/cm^{-1} (KBr) 2923, 1714, 1481, 1461, 1438, 1373, 1342, 1316, 1247, 1160, 1093, 745, 596, 527; UV−vis (CHCl$_3$) λ_{max}/nm (log ε) 256 (4.93), 313 (4.61), 426 (3.40), 686 (2.25); MALDI FT-ICR MS *m*/*z* calcd for $C_{69}H_9NO_2$ [M$^-$] 883.0633, found 883.0637.

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Supporting Information Available: Spectral data of **2b**−**d** and **2f**, **g** along with the NMR spectra of **2a**−**g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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