行政院國家科學委員會補助專題研究計畫 □成果報告 ■期中進度報告

合成具開口碳六十及內包氫氣、氦氣與釓離子之化學反應探討

計畫類別：■ 個別型計畫　　□ 整合型計畫
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執行單位：國立交通大學應用化學系

中　華　民　國　99　年　05　月　31　日

（一） 計畫中文摘要

由於具開口碳六十之分子容器無法以傳統的電弧放電方式獲得，目前只能依賴有機合成方式。本計劃實行的重點在於以合成方法達到含氫氣、氨氣與釓金屬離子之開口碳六十為方向，以應用於儲氫、儲氨之分子容器及應用於內包釓金屬離子做為核磁共振顯影劑。此計劃第一階段將探討以有機金屬催化合成反應獲得具開口之碳六十衍生物，例如以鎳金屬催化碳六十環化反應。第二階段為探討將具有開口碳六十衍生物，以化學方法形成一個大的開口，再置入氫氣與氨氣。

關鍵詞: 碳六十、開口碳六十、分子容器、氫氣、氨氣、金屬催化

（二） 計畫英文摘要。

Organic synthesis of open-cage fullerenes containing hydrogen, ammonia and gadolinium inside the cage is described. The desire for these endohedral open-cage fullerenes is primarily driven from their potentialities as hydrogen or ammonia-container in the frontier material field and superior magnetic resonance imaging agent in biomedical field. The availability of these compounds has yet to rely on organic synthesis because they can not be obtained from conventional electrical arc discharge method. The described approach herein starts from metal-catalyzed cycloaddition with C_{60}. A large opening will be formed by controlled bond scissions. The synthesized open-cage fullerenes can be molecular containers that will be inserted hydrogen or ammonia at high pressure.

Keyword: C_{60}, open-cage fullerene, molecular container, hydrogen, ammonia, metal-catalysis

（二）報告內容

Introduction

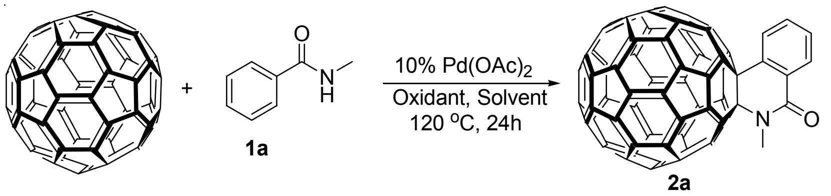
Fullerene materials remain one of the good candidate materials for resolving issues with energy. Fullerenes can be modified chemically to form an opening and subsequently inserted with guest molecules as hydrogen, insertion of other large guest molecules as ammonia or methane could be possible. The desire for larger opening on fullerenes remains highly demanded for study of encapsulation of larger species. In the first term of this project, we investigate metal catalyzed functionalization for derivatizing C_{60} for future opening on C_{60} through synthetic approach by merging two chemically-opened holes.

Results and discussion

We have found a palladium-catalyzed annulation of benzamides with C_{60}. First, we synthesized the N-alkylated benzamides **1a**–**j** according to conventional methods. We used *N*-methylbenzamide (**1a**) as a standard substrate for our optimization studies. Initially, we evaluated the reaction of C_{60} (36 mg, 0.050 mmol) with **1a** (20 mg, 0.15 mmol) in the presence of $Pd(OAc)_2$ (1.1 mg, 0.0050 mmol, 10%) and oxone (22 mg, 0.15 mmol) in *o*-DCB/TFA (6:1, v/v;

7 mL) at 120 °C in a sealed tube for 24 h; we obtained the desired C_{60}-fused isoquinolinone **2a** in 33% isolated yield, 45% based on recovered C_{60} (Table 1, entry 1). Although the formation of this fulleroisoquinolinone was relatively efficient under these conditions, we explored reactions using other oxidizing agents and solvents in a quest for better yields. The corresponding reactions performed using the common oxidants $Cu(OAc)_2$, CH_3COOAg,[1] and Ag_2O,[2] under the standard conditions described above, improved the yields of **2a** to 50, 45, and 38%, respectively (Table 1, entries 3–5). Next, we tested the catalytic reaction using AcOH,[3] DMSO,[4] CH_3CN,[5] and 1-chloronaphthalene as co-solvents, but the resulting transformations were relatively less efficient (entries 6–10). The reactions performed in chlorobenzene/TFA (10:1) gave **2a** in 42% yield with only a trace amount of recovered C_{60} (entry 11). The addition of one equiv. of water deteriorated the reaction performance (entry 12).

Table 1. Reactions of C_{60} with **1a** Under Various Conditions



entry	oxidant	solvents (mL)	Yield (%)[b]
1	Oxone	*o*-DCB/TFA (6:1)	33 (45)
2	Oxone	*o*-DCB/DMSO(6:1)	7 (32)
3	$Cu(OAc)_2$	*o*-DCB/TFA (6:1)	50 (84)
4	CH_3COOAg	*o*-DCB/TFA (6:1)	45 (85)
5	Ag_2O	*o*-DCB/TFA (6:1)	38 (53)
6	$Cu(OAc)_2$	*o*-DCB/AcOH (6:1)	4 (10)
7	Cu(OAc)	*o*-DCB/DMSO (6:1)	<3
8	$Cu(OAc)_2$	*o*-DCB/CH_3CN (6:1)	<3
9	CH_3COOAg	*o*-DCB/AcOH (6:1)	5 (12)
10	$Cu(OAc)_2$	1-Cl-naphthalene/TFA (6:1)	14 (86)
11	$Cu(OAc)_2$	PhCl/TFA(10:1)	42
12[c]	$Cu(OAc)_2$	*o*-DCB/TFA (6:1)	37 (55)

We further evaluated the catalytic scope of this system by employing a variety of substrates **1b**–**j** (Table 2) featuring either electron-donating and -withdrawing groups on their benzamide aryl ring. In general, substrates equipped with electron-donating groups afforded their corresponding fulleroisoquinolinones in good yields (Table 2, entries 4–7). Substrates **1e** and **1f** underwent regioselective C–H activations[7] at their less-hindered and more-electron-rich para positions (relative to their Me substituents) to afford **2e** and **2f** in excellent yields of 63 and 61%, respectively (Table 2, entries 5 and 6). Substrates bearing electron-withdrawing groups, such as the chloro and phenyl units of **1h**–**j**, provided their products in only moderate yields (Table 2, entries 8–10). Under the standard conditions, the reactions of amides bearing N-benzyl substituents (**1c**, **1d**, **1g**, **1j**) yielded debenzylated products. To overcome this problem, we

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(1) (a) Shabashov, D.; Molina Maldonado, J. R.; Daugulis, O. *J. Org. Chem.* **2008**, *73*, 7818–7821. (b) Daugulis, O.; Zaitsev, V. G. *Angew. Chem., Int. Ed.* **2005**, *44*, 4046–4048.

(2) Thirunavukkarasu, V. S.; Parthasarathy, K.; Cheng, C. H. *Angew.Chem. Int. Ed.* **2008**, *47*, 9462–9465.

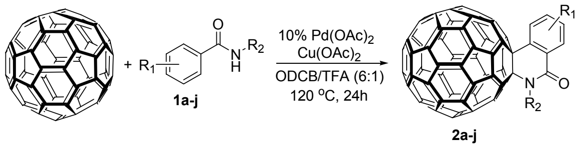
(3) Kalyani, D.; Deprez, N. R.; Desai, L. V.; Sanford, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 7330–7331.

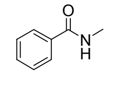
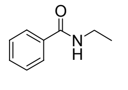
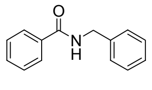
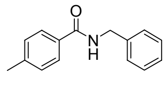
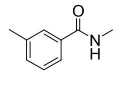
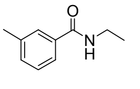
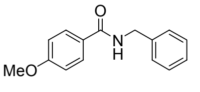
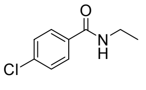
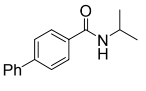
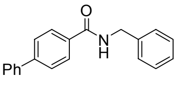
(4) Inamoto, K.; Saito, T.; Katsuno, M.; Sakamoto, T.; Hiroya, K. *Org. Lett.* **2007**, *9*, 2931–2934.

(5) Chen, X.; Li, J. J.; Hao, X. S.; Goodhue, C. E.; Yu, J. Q. *J. Am. Chem. Soc.* **2006**, *128*, 78–79.

performed these experiments using only 0.2 mL of TFA, obtaining the desired products in moderate yields (Table 2, entries 3, 4, 7, and 10).

Table 2. Palladium-Catalyzed Syntheses of the Fulleroisoquinolinones **2a–j**



entry	amide **1**	product	yield (%)	recovered C_{60} (%)
1		**2a**	50 (84)	42
2		**2b**	72 (78)	8
3		**2c**	30 (39)	22
4		**2d**	34 (62)	44
5		**2e**	63	trace
6		**2f**	61 (84)	28
7^c		**2g**	40 (76)	47
8		**2h**	31 (56)	44
9		**2i**	20 (48)	55
10		**2j**	24 (41)	42

We characterized the fulleroisoquinolinones **2a–j** using infrared (IR) and ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, fast atom bombardment mass spectrometry (FAB MS), and X-ray crystallography. Because each of these compounds possesses a symmetrical plane, its ^{13}C NMR spectrum exhibits 30 sp^2-hybridized carbon atoms on the C_{60} cage. In their IR spectra, C=O stretching bands appear at ca. 1650 cm^{-1}. Figure 1 displays a 2D-HMBC spectrum of the selected compound **2f**. We made partial peak assignments on the basis of one- (2D-HMQC) and three-bond (2D-HMBC) correlation spectra. For example, the sp^3-hybridized carbon atoms of the C_{60} moiety of **2f** appear as two signals at 62.60 (C1) and 79.29 (C2) ppm; C1 and C2 correlate with the protons on C6 and C11, respectively, through three-bond couplings. Figure 2 presents the structure of compound **2d** determined using X-ray diffraction analysis.

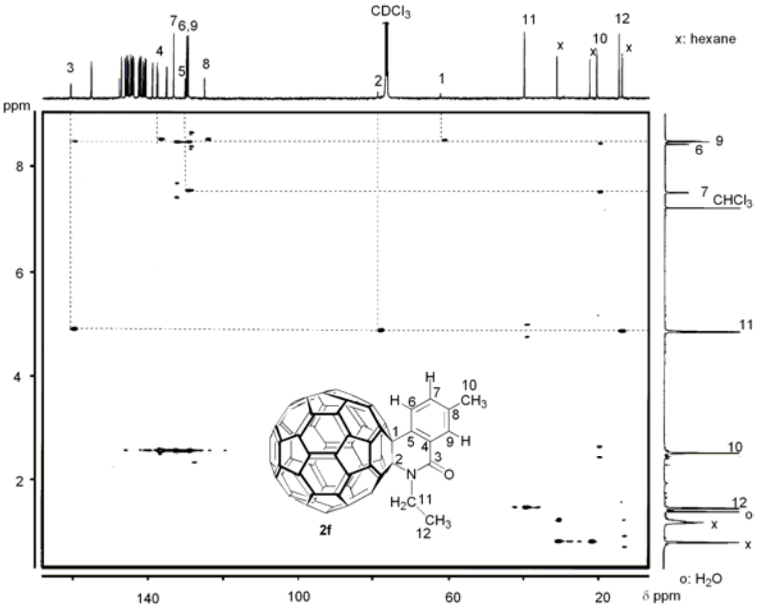


Figure 1. 2D-HMBC spectrum of compound **2f**.

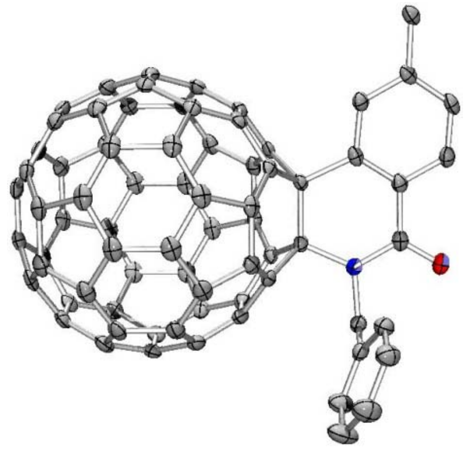


Figure 2. X-ray crystal structure of compound **2d**.

Conclusion

we have achieved metal-catalyzed functionalization in the first step, our next goal will be extending this type of molecule toward opening. The following work is under progress using debenzylated compounds..