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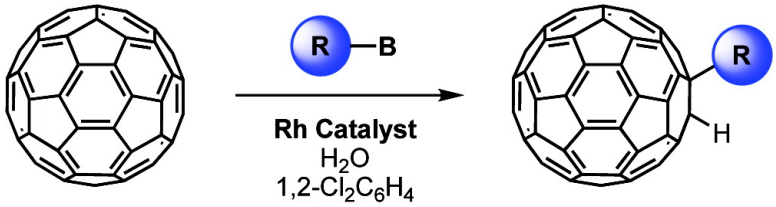

R = aryl, heteroaryl, alkenyl
B = $B(OH)_2$, B(pin), BF_3K

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Rh-Catalyzed Arylation and Alkenylation of C_{60} Using Organoboron Compounds

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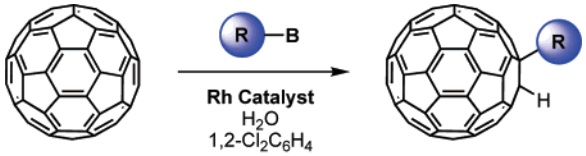
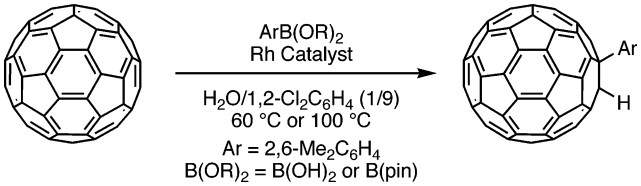
Functionalized fullerenes have attracted significant attention as promising structural/functional units in nanoscience.[1] To this end, a number of chemical reactions of fullerenes have been developed, such as different types of cycloaddition and the addition of nucleophiles and free radicals.[1] The addition of organometallic compounds, such as organolithiums or Grignard reagents, is one such classical reaction in fullerene chemistry.[2] Although these addition reactions have contributed significantly to the generation of interesting nanostructures,[3] as exemplified by Nakamura's multifold addition of organocopper reagents, there remains considerable room for further investigations, giving that (i) high loading of organometallic reagents is typically required, (ii) selective monoaddition is often difficult, (iii) functional group compatibility is relatively low, and (iv) the use of metal catalysis, which offers various opportunities for selectivity control, has not been forthcoming. A key to addressing these issues is to generate a reasonably nucleophilic but functional-group-compatible organometallic species in a catalytic manner. Inspired by recent progress in rhodium-catalyzed reaction of organoboron compounds with various electrophiles, such as electron-deficient alkenes and alkynes,[4] as well as by the general disposition of C_{60} as an electron acceptor,[1] we envisioned the rhodium-catalyzed functionalization of C_{60} using organoboron compounds.[5]



In early experiments, we found that 2,6-dimethylphenylboronic acid possesses reasonable reactivity toward C_{60}. For example, when a mixture of the boronic acid and C_{60} was treated with a catalytic amount of $[RhCl(cod)]_2$ (cod = 1,5-cyclooctadiene) in H_2O/1,2-$Cl_2C_6H_4$ (1/9) at 60 °C for 3 h (molar ratio, C_{60}/ArB(OH)$_2$/Rh = 1:2:0.1), a hydroarylation adduct was obtained in 27% yield with 90% selectivity[6] (Table 1, entry 1, left column). The hydroarylation took place across the C=C bond between two six-membered rings of C_{60}.

On the basis of this preliminary result, we set out to investigate the effect of rhodium(I) complexes with this model substrate (Table 1). All reactions were stopped after 3 h to ensure appropriate comparison of catalytic activities. The use of $[RhOH(cod)]_2$ gave rise to higher yield (57%), but this was achieved at the expense of low selectivity (66%); multiple addition products were detected by LCMS analysis. When $[Rh(cod)_2]BF_4$ was used, both a good yield (61%) and excellent selectivity (>95%) were achieved. However, other representative cationic complexes, such as $[Rh(cod)_2]PF_6$ and

Table 1. Catalyst Screening and Reaction Optimization[a]



		boronic acid		pinacol ester	
entry	catalyst	yield[b]	selectivity[c]	yield[b]	selectivity[c]
1	$[RhCl(cod)]_2$	27%	90%	–	–
2	$[RhOH(cod)]_2$	57%	66%	19%	68%
3	$[Rh(cod)_2]BF_4$	61%	>95%	25%	78%
4	$[Rh(cod)_2]PF_6$	<1%	–	14%	88%
5	$[Rh(cod)_2]OTf$	<1%	–	14%	88%
6	$[Rh(nbd)_2]BF_4$	17%	>95%	–	–
7	$[Rh(cod)(MeCN)_2]BF_4$	67%	88%	60%	>95%
8[d]	$[Rh(cod)(MeCN)_2]BF_4$	84%	91%	–	–
9[d,e]	$[Rh(cod)(MeCN)_2]BF_4$	80%	>95%	–	–
10[d,f]	$[Rh(cod)(MeCN)_2]BF_4$	68%	>95%	–	–

[a] Molar ratio: C_{60}/ArB(OR)$_2$/Rh = 1:2:0.1. Conditions: 60 °C, 3 h (boronic acid); 100 °C, 10 h (pinacol ester). [b] Conversion of C_{60} and yield of product were determined by HPLC analysis using C_{70} as an internal standard. [c] Determined by [yield of product]/[conversion of C_{60}]. [d] H_2O/1,2-$Cl_2C_6H_4$ = 1:4. [e] C_{60}/ArB(OR)$_2$/Rh = 1:1.2:0.1. [f] C_{60}/ArB(OR)$_2$/Rh = 1:1.2:0.05.

$[Rh(cod)_2]OTf$, were found to be totally inactive. These results were surprising because it has been well-documented that these complexes behave similarly in standard catalytic transformations. However, any speculation regarding this dramatic counteranion effect must await further mechanistic investigations. Changing the diene ligand from cod to norbornadiene (nbd) resulted in lower reactivity (entry 6), indicating that at least one of the dienes dissociates from rhodium before becoming catalytically active. In line with this assumption, the use of $[Rh(cod)(MeCN)_2]BF_4$ resulted in a 67% yield with 88% selectivity (entry 7). We further found that increasing the amount of water (H_2O/1,2-$Cl_2C_6H_4$ = 1/4) allowed an 84% yield (entry 8). Under these conditions, the amount of ArB(OH)$_2$ and Rh complex could be reduced to 1.2 and 0.05 equiv, respectively (entries 9 and 10).

We also examined the reactivity of these rhodium complexes with the corresponding pinacol ester (Table 1, right column). Because the reactivity of pinacol ester is generally lower than that of boronic acid, the reactions were conducted at 100 °C. The general trend was found to be similar to that obtained with the reactions of boronic acid. Thus, we identified $[Rh(cod)(MeCN)_2]BF_4$ as our first-choice standard catalyst precursor for the reaction of C_{60}.

With a first-generation procedure in hand, we next examined the reaction with several organoboron compounds in order to gain a rough grasp of the scope of the present rhodium catalysis (Table 2). The reaction took place with various electronically and

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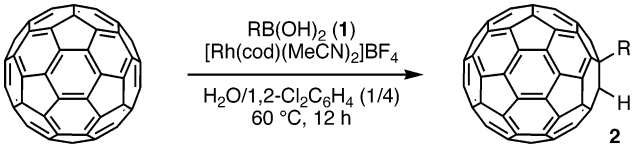
Table 2. Rh-Catalyzed Arylation and Alkenylation to C_{60} Using Organoboron Compounds[a]



entry	RB(OH)$_2$ (**1**)	**2**	conv[b]	yield[c]	selectivity[d]
1	$C_6H_5B(OH)_2$ (**1a**)	**2a**	47%	45% (40%)	>95%
2	4-Me$C_6H_4B(OH)_2$ (**1b**)	**2b**	50%	49% (40%)	>95%
3[e,f]	2-Me$C_6H_4B(OH)_2$ (**1c**)	**2c**	64%	53% (46%)	83%
4[f]	2,6-$Me_2C_6H_3B(OH)_2$ (**1d**)	**2d**	80%	80% (69%)	>95%
5	4-Cl$C_6H_4B(OH)_2$ (**1e**)	**2e**	38%	38% (32%)	>95%
6	4-MeO$C_6H_4B(OH)_2$ (**1f**)	**2f**	52%	45% (35%)	87%
7	4-MeO$C_6H_4BF_3K$ (**1f′**)	**2f**	62%	51% (43%)	82%
8[g]	4-MeC(O)$C_6H_4B(OH)_2$ (**1g**)	**2g**	47%	47% (42%)	>95%
9[e,f]	1-naphthylB$(OH)_2$ (**1h**)	**2h**	68%	55% (51%)	81%
10[e,f]	1-pyrenylB$(OH)_2$ (**1i**)	**2i**	69%	56% (49%)	81%
11[h]	(*E*)-C_6H_5CH=$CHBF_3K$ (**1j′**)	**2j**	51%	36% (34%)	67%
12[g]	3-thienylB$(OH)_2$ (**1k**)	**2k**	53%	53% (48%)	>95%

[a] Molar ratio: C_{60}/**1**/Rh = 1:1.5:0.1. [b] Conversion of C_{60} determined by HPLC using C_{70} as an internal standard. [c] Yield of **2** determined by HPLC using C_{70} as an internal standard. The number in parenthesis is the isolated yield. [d] Selectivities were determined by [yield of **2**]/[conversion of C_{60}]. [e] Reactions conducted at room temperature. [f] C_{60}/**1**/Rh = 1:1.2:0.1. [g] [RhOH(cod)]$_2$ was used. [h] H_2O/1,2-$Cl_2C_6H_4$ = 1:9.

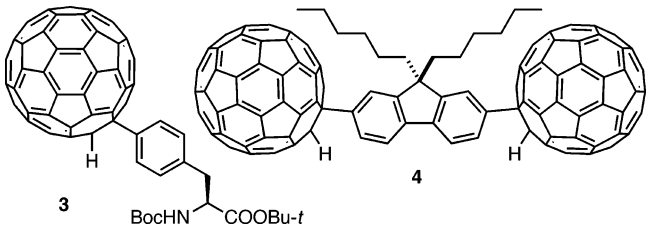


Figure 1. Other representative functionalized fullerenes.

structurally diverse boronic acids. In all cases examined, selectivity was good to excellent. Functional groups, such as the acetyl group, which usually cannot be applied in the existing organometallic additions, have been found to be compatible (entry 8).[7] Extended π-systems such as naphthyl, pyrenyl, and styryl groups can also be introduced (entries 9−11). Although some heteroarylboronic acids, such as 3-thienylboronic acid, possessed low reactivity, the use of highly reactive [RhOH(cod)]$_2$ was found to be a solution for such sluggish reagents (entry 12). The use of potassium trifluoro(organo)borates gave better results in some cases (entries 6 and 7).[8] A moderate electronic effect of the aryl group was observed for the reaction efficiency, but we unexpectedly found that ortho-substituted **1c** and **1d** reacted markedly faster than the other arylboronic acids.[9]

Other functionalized fullerenes were also created by the present rhodium catalysis (Figure 1; see Supporting Information for details). For example, when protected phenylalanine equipped with the $B(OH)_2$ group was reacted, a fullerene-tagged amino acid **3** was obtained. This may be useful for various biological applications.[1] When 9,9-dihexylfluorene-2,7-diboronic acid was reacted with 2 molar amounts of C_{60}, two-directional reaction occurred, yielding an interesting fullerene-capped π-system **4**.

In summary, we have established a new organoboron-based arylation and alkenylation of C_{60} catalyzed by a rhodium complex. The described chemistry not only broadens the scope of the functionalization chemistry of fullerenes, thereby providing a new synthetic avenue to a wide variety of previously unexplored fullerene-based materials, but also represents a new direction for molecular catalysis in nanocarbon chemistry.[10] Work along this line, as well as the development of a more efficient catalyst, is ongoing.

Acknowledgment. This paper is dedicated to the memory of Professor Yoshihiko Ito. Support has been provided in part by PRESTO, Japan Science and Technology Agency (JST).

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

References

(1) (a) Hirsch, A.; Brettreich, M. *Fullerenes: Chemistry and Reactions*; Wiley-VCH: Weinheim, Germany, 2005. (b) Kadish, K. M., Ruoff, R. S., Eds. *Fullerenes: Chemistry, Physics, and Technology*; Wiley: New York, 2000. (c) Martin, N. *Chem. Commun.* **2006**, 2093.

(2) (a) Wudl, F.; Hirsch, A.; Khemani, K. C.; Suzuki, T.; Allemand, P. M.; Kosch, A.; Eckert, H.; Srdanov, G.; Webb, H. M. ACS Symposium Series 481; American Chemical Society: Washington, DC, 1992; p 161. (b) Hirsch, A.; Soi, A.; Karfunkel, H. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 766. (c) Fagan, P. J.; Krusic, P. J.; Evans, D. H.; Lerke, S. A.; Johnston, E. *J. Am. Chem. Soc.* **1992**, *114*, 9697. (d) Hirsch, A.; Grösser, T.; Skiebe, A.; Soi, A. *Chem. Ber.* **1993**, *126*, 1061. (e) Nagashima, H.; Terasaki, H.; Kimura, E.; Nakajima, K.; Itoh, K. *J. Org. Chem.* **1994**, *59*, 1246. (f) Komatsu, K.; Murata, Y.; Takimoto, N.; Mori, S.; Sugita, N.; Wan, T. S. M. *J. Org. Chem.* **1994**, *59*, 6101. (g) Sawamura, M.; Iikura, H.; Nakamura, E. *J. Am. Chem. Soc.* **1996**, *118*, 12850. (h) Matsuo, Y.; Tahara, K.; Morita, K.; Matsuo, K.; Nakamura, E. *Angew. Chem., Int. Ed.* **2007**, *46*, 2844.

(3) Examples: (a) Zhou, S.; Burger, C.; Chu, B.; Sawamura, M.; Nagahama, N.; Toganoh, M.; Hackler, U. E.; Isobe, H.; Nakamura, E. *Science* **2001**, *291*, 1944. (b) Sawamura, M.; Kawai, K.; Matsuo, Y.; Kanie, K.; Kato, T.; Nakamura, E. *Nature* **2002**, *419*, 702. (c) Murata, Y.; Ito, M.; Komatsu, K. *J. Mater. Chem.* **2002**, *12*, 2009. (d) Matsuo, Y.; Tahara, K.; Sawamura, M.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, *126*, 8725. (e) Yamazaki, T.; Murata, Y.; Komatsu, K.; Furukawa, K.; Morita, M.; Maruyama, N.; Yamao, T.; Fujita, S. *Org. Lett.* **2004**, *6*, 4865. (f) Zhong, Y.-W.; Matsuo, Y.; Nakamura, E. *Org. Lett.* **2006**, *8*, 1463. (g) Zhong, Y.-W.; Matsuo, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2007**, *129*, 3052.

(4) Pioneering works: (a) Sakai, M.; Hayashi, H.; Miyaura, N. *Organometallics* **1997**, *16*, 4229. (b) Takaya, Y.; Ogasawara, M.; Hayashi, T.; Sakai, M.; Miyaura, N. *J. Am. Chem. Soc.* **1998**, *120*, 5579. Reviews: (c) Fagnou, K.; Lautens, M. *Chem. Rev.* **2003**, *103*, 169. (d) Hayashi, T.; Yamasaki, K. *Chem. Rev.* **2003**, *103*, 2829. Selected recent examples in this area: (e) Paquin, J.-F.; Defieber, C.; Stephenson, C. R. J.; Carreira, E. M. *J. Am. Chem. Soc.* **2005**, *127*, 10850. (f) Tseng, N.-W.; Mancuso, J.; Lautens, M. *J. Am. Chem. Soc.* **2006**, *128*, 5338. (g) Shintani, R.; Duan, W.-L.; Hayashi, T. *J. Am. Chem. Soc.* **2006**, *128*, 5628. (h) Tonogaki, K.; Itami, K.; Yoshida, J. *Org. Lett.* **2006**, *8*, 1419. (i) Miura, T.; Murakami, M. *Chem. Commun.* **2007**, 217. (j) Walter, C.; Auer, G.; Oestreich, M. *Angew. Chem., Int. Ed.* **2007**, *45*, 5675. (k) Kurahashi, T.; Shinokubo, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 6336. (l) Uehara, K.; Miyamura, S.; Satoh, T.; Miura, M. *J. Organomet. Chem.* **2006**, *691*, 2821. (m) Ukai, K.; Aoki, M.; Takaya, J.; Iwasawa, N. *J. Am. Chem. Soc.* **2006**, *128*, 8706.

(5) Boronic acid derivatives are air-stable, storable, and easily accessible by various methods. For general views for boronic acid derivatives, see: Hall, D. G., Ed. *Boronic Acids*; Wiley-VCH: Weinheim, Germany, 2005. Over 750 boronic acid derivatives are now commercially available from Sigma-Aldrich (http://www.sigmaaldrich.com).

(6) Throughout this paper, "selectivity" stands for a ratio of the quantity of desired product over the quantity of substrate converted (Orchin, M.; Macomber, R. S.; Pinhas, A. R.; Wilson, R. M., *The Vocabulary and Concepts of Organic Chemistry*, 2nd ed.; Wiley-Interscience: New Jersey, 2005).

(7) For an exception in this regard, see ref 3f.

(8) Potassium trifluoro(organo)borates in rhodium-catalyzed conjugate additions: (a) Navarre, L.; Pucheault, M.; Darses, S.; Genet, J.-P. *Tetrahedron Lett.* **2005**, *46*, 4247. (b) Duursma, A.; Boiteau, J.-G.; Lefort, L.; Boogers, J. A. F.; de Vries, A. H. M.; de Vries, J. G.; Minnaard, A. J.; Feringa, B. L. *J. Org. Chem.* **2004**, *69*, 8045. (c) Moss, R. J.; Wadsworth, K. J.; Chapman, C. J.; Frost, C. G. *Chem. Commun.* **2004**, 1984.

(9) Recently, Hartwig also found a similar ortho-substitution effect in transmetalation from boron to rhodium, which might be closely related to the present reaction: (a) Zhao, P.; Incarvito, C. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2007**, *129*, 1876. Kakiuchi also observed a seemingly similar effect in ruthenium catalysis using arylboronates: (b) Kakiuchi, F.; Matsuura, Y.; Kan, S.; Chatani, N. *J. Am. Chem. Soc.* **2005**, *127*, 5936.

(10) Catalytic modification of C_{60}: (a) Becker, L.; Evans, T. P.; Bada, J. L. *J. Org. Chem.* **1993**, *58*, 7630. (b) Shiu, L.-L.; Lin, T.-I.; Peng, S.-M.; Her, G.-R.; Ju, D. D.; Lin, S.-K.; Hwang, J.-H.; Mou, C. Y.; Luh, T.-Y. *J. Chem. Soc., Chem. Commun.* **1994**, 647. (c) Shen, C. K. F.; Chien, K.-M.; Liu, T.-Y.; Lin, T.-I.; Her, G.-R.; Luh, T.-Y. *Tetrahedron Lett.* **1995**, *36*, 5383. (d) Gan, L.; Huang, S.; Zhang, X.; Zhang, A.; Cheng, B.; Cheng, H.; Li, X.; Shang, G. *J. Am. Chem. Soc.* **2002**, *124*, 13384. For catalytic transformation of functionalized fullerenes, see: (e) Matsuo, Y.; Iwashita, A.; Nakamura, E. *Chem. Lett.* **2006**, *35*, 858.

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