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Fullerenyl Boronic Esters: Ferric Perchlorate-Mediated Synthesis and Functionalization

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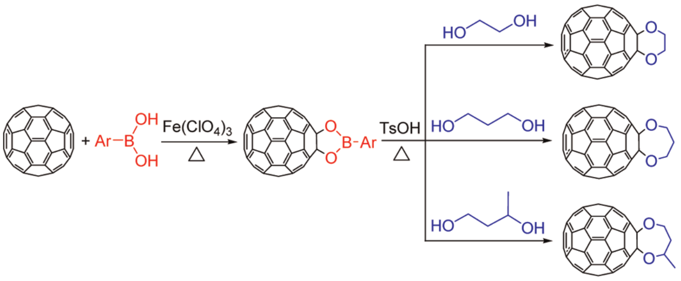
ABSTRACT



Fullerenyl boronic esters have been prepared by a ferric perchlorate-promoted reaction of [60]fullerene with various arylboronic acids. The obtained fullerenyl boronic esters could undergo further functionalization with diols to afford C_{60}-fused dioxane/dioxepane derivatives. A possible reaction mechanism for the formation of fullerenyl boronic esters has been proposed.

Since fullerenes have become available in macroscopic amounts, numerous chemical reactions of fullerenes have been developed to prepare a plethora of functionalized fullerene derivatives.[1] Various reactions of fullerenes catalyzed or mediated by transition-metal salts, particularly those of Pd,[2] Rh,[3] and Mn,[4] have attracted extensive attention.[5] Organoboron compounds have been widely used in organic synthesis.[6] Itami and co-workers recently reported the Pd-catalyzed arylation of [60]fullerene (C_{60}) with arylboronic acids.[2d] Itami's group also developed the Rh-catalyzed arylation and alkenylation of C_{60} using

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(1) For selected reviews, see: (a) Hirsch, A. *Synthesis* **1995**, 895. (b) Thilgen, C.; Diederich, F. *Chem. Rev.* **2006**, *106*, 5049. (c) Giacalone, F.; Martín, N. *Chem. Rev.* **2006**, *106*, 5136. (d) Matsuo, Y.; Nakamura, E. *Chem. Rev.* **2008**, *108*, 3016. (e) Murata, M.; Murata, Y.; Komatsu, K. *Chem. Commun.* **2008**, 6083.

(2) Pd: (a) Shiu, L.-L.; Lin, T.-I.; Peng, S.-M.; Her, G.-R.; Ju, D.-D.; Lin, S.-K.; Hwang, J.-H.; Mon, C.-Y.; Luh, T.-Y. *J. Chem. Soc., Chem. Commun.* **1994**, 647. (b) Shen, C. K. F.; Chien, K.-M.; Liu, T.-Y.; Lin, T.-I.; Her, G.-R.; Luh, T.-Y. *Tetrahedron Lett.* **1995**, *36*, 5383. (c) Inoue, H.; Yamaguchi, H.; Suzuki, T.; Akasaka, T.; Murata, S. *Synlett* **2000**, 1178. (d) Mori, S.; Nambo, M.; Chi, L.-C.; Bouffard, J.; Itami, K. *Org. Lett.* **2008**, *10*, 4609. (e) Nambo, M.; Itami, K. *Chem.—Eur. J.* **2009**, *15*, 4760. (f) Zhu, B.; Wang, G.-W. *J. Org. Chem.* **2009**, *74*, 4426. (g) Zhu, B.; Wang, G.-W. *Org. Lett.* **2009**, *11*, 4334. (h) Nambo, M.; Wakamiya, A.; Yamaguchi, S.; Itami, K. *J. Am. Chem. Soc.* **2009**, *131*, 15112. (i) Chuang, S.-C.; Rajeshkumar, V.; Cheng, C.-A.; Deng, J.-C.; Wang, G.-W. *J. Org. Chem.* **2011**, *76*, 1599. (j) Chen, C.-P.; Luo, C.; Ting, C.; Chuang, S.-C. *Chem. Commun.* **2011**, *47*, 1845.

(3) Rh: (a) Becker, L.; Evans, T. P.; Bada, J. L. *J. Org. Chem.* **1993**, *58*, 7630. (b) Gonzalez, R.; Knight, B. W.; Wudl, F. *J. Org. Chem.* **1994**, *59*, 7949. (c) Pellicciari, R.; Annibali, D.; Costantino, G.; Marinozzi, M.; Natalini, B. *Synlett* **1997**, 1196. (d) Duczek, W.; Radeck, W.; Niclas, H.-J.; Ramm, M.; Costisella, B. *Tetrahedron Lett.* **1997**, *38*, 6651. (e) Nair, V.; Sethumadhavan, D.; Sheela, K. C.; Eigendorf, G. K. *Tetrahedron Lett.* **1999**, *40*, 5087. (f) Muraoka, T.; Asaji, H.; Yamamoto, Y.; Matsuda, I.; Itoh, K. *Chem. Commun.* **2000**, 199. (g) Nair, V.; Sethumadhavan, D.; Sheela, K. C.; Nair, S. M.; Eigendorf, G. K. *Tetrahedron* **2002**, *58*, 3009. (h) Nambo, M.; Noyori, R.; Itami, K. *J. Am. Chem. Soc.* **2007**, *129*, 8080. (i) Nambo, M.; Segawa, Y.; Wakamiya, A.; Itami, K. *Chem. Asian J.* **2011**, *6*, 590.

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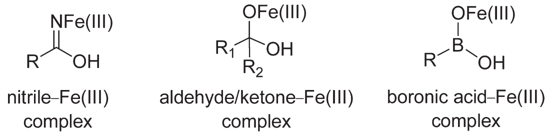
organoboron compounds.[3h,i] They later extended the Rh-catalyzed arylation to [70]fullerene (C_{70}).[3i] *p*-Tolylboronic acid was also employed to functionalize *N*-tosyl[1,2]-aziridino[60]fullerene affording the corresponding fullerenyl boronic ester, and the aziridinofullerene was in turn synthesized by the aziridination of C_{60} with TsN=IPh.[5e] This was the only known example of fullerene diols protected as a boronic ester. We previously disclosed the reactions of C_{60} with nitriles, aldehydes/ketones, and malonate esters mediated by cheap $Fe(ClO_4)_3$ to afford C_{60}-fused oxazolines,[7a] C_{60}-fused 1,3-dioxolanes,[7b] and C_{60}-fused disubstituted lactones,[7c] respectively. The reactions of C_{60} with nitriles[7a] and aldehydes/ketones[7b] were believed to proceed via the $Fe(ClO_4)_3$-mediated hydration reaction to generate Fe(III) complexes **I** and **II**, respectively (Figure 1). We conjectured that boronic acids might coordinate with $Fe(ClO_4)_3$ to form Fe(III) complex **III**, which could similarly react with C_{60} and provide the scare fullerenyl boronic esters in one pot. Herein, we report our success in the synthesis of fullerenyl boronic esters by the $Fe(ClO_4)_3$-mediated reaction of C_{60} with arylboronic acids and further conversion into C_{60}-fused dioxane/dioxepane derivatives.



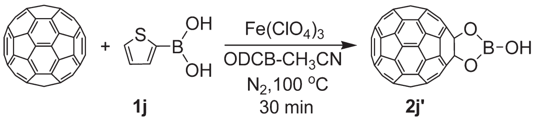
I **II** **III**

Figure 1. Proposed reaction intermediates.

To our satisfaction, $Fe(ClO_4)_3$ efficiently promoted the reaction of C_{60} with a series of arylboronic acids (**1a**–**i**) to generate the expected fullerenyl boronic esters. The reaction conditions and yields for the $Fe(ClO_4)_3$-promoted reaction of C_{60} with **1a**–**i** are listed in Table 1. As can be seen from Table 1, fullerenyl boronic esters **2a**–**i** were obtained in 13–38% yields (57–93% based on consumed C_{60}), comparable to the previously reported data for most monoadducts. Control experiments in the absence of $Fe(ClO_4)_3$ or heating gave no desired products. It should be noted that although no bis-adducts could be isolated, some unknown highly polar byproducts were formed in some cases. The current reaction was compatible with a wide variety of functional groups such as bromo, keto, cyano, and nitro groups, which may be used as synthetic handles for further functionalization. Unfortunately, no or only trace amounts of fullerenyl boronic esters could be obtained for arylboronic acids bearing electron-donating groups such as 4-methylphenylboronic acid and 4-methoxyphenylboronic acid as well as alkyl boronic acids such as isopropyl boronic acid even in the presence of excess of reaction reagents or by increasing the reaction temperature and extending the reaction time.

It is noteworthy that the $Fe(ClO_4)_3$-promoted reaction of C_{60} with thiophene-2-boronic acid (**1j**) under the same conditions produced fullerenyl borate ester **2j′** in 32% isolated yield (94% based on consumed C_{60}), instead of the expected fullerenyl boronic ester **2j** (Scheme 1).

Scheme 1. $Fe(ClO_4)_3$-Mediated Reaction of C_{60} with Thiophene-2-boronic Acid **1j**



Fullerenyl boronic esters **2a**–**i** and borate **2j′** were characterized by HRMS, ^1H NMR, ^{13}C NMR, FT-IR, and UV–vis spectra. All of the ^1H NMR spectra exhibited the corresponding expected signals. In the ^{13}C NMR spectra of **2a**–**i** and **2j′**, there were no more than 16 lines in the range of 136–149 ppm for the 58 sp^2-carbons of the C_{60} skeleton and one peak at 92–96 ppm for the two sp^3-carbons of the C_{60} cage, agreeing well with their C_{2v} molecular symmetry. The observed chemical shifts at 92–96 ppm are close to those of other 1,2-adducts, of which the oxygen atom is connected to the C_{60} skeleton.[4h–j,7]

On the basis of the previously suggested mechanisms for the reactions of C_{60} with nitriles[7a] and aldehydes/ketones[7b] in the presence of $Fe(ClO_4)_3$, we propose a possible mechanism for the formation of fullerenyl boronic esters **2** from the $Fe(ClO_4)_3$-mediated reaction of C_{60} with boronic acids (Scheme 2). A chosen boronic acid reacts with $Fe(ClO_4)_3$ to produce Fe(III) complex **III** accompanied by the elimination of $HClO_4$. Addition of complex **III** to C_{60} generates fullerenyl radical **IV**, followed by coordination with another molecule of $Fe(ClO_4)_3$ to form Fe(III)

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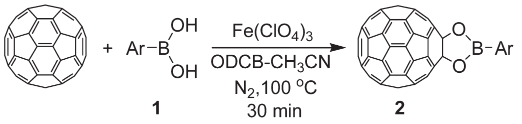
(4) Mn: (a) Zhang, T.-H.; Lu, P.; Wang, F.; Wang, G.-W. *Org. Biomol. Chem.* **2003**, *1*, 4403. (b) Wang, G.-W.; Zhang, T.-H.; Cheng, X.; Wang, F. *Org. Biomol. Chem.* **2004**, *2*, 1160. (c) Li, C.; Zhang, D.; Zhang, X.; Wu, S.; Gao, X. *Org. Biomol. Chem.* **2004**, *2*, 3464. (d) Wang, G.-W.; Li, F.-B. *Org. Biomol. Chem.* **2005**, *3*, 794. (e) Chen, Z.-X.; Wang, G.-W. *J. Org. Chem.* **2005**, *70*, 2380. (f) Cheng, X.; Wang, G.-W.; Murata, Y.; Komatsu, K. *Chin. Chem. Lett.* **2005**, *16*, 1327. (g) Wang, G.-W.; Yang, H.-T.; Miao, C.-B.; Xu, Y.; Liu, F. *Org. Biomol. Chem.* **2006**, *4*, 2595. (h) Wang, G.-W.; Li, F.-B.; Zhang, T.-H. *Org. Lett.* **2006**, *8*, 1355. (i) Li, F.-B.; Liu, T.-X.; Huang, Y.-S.; Wang, G.-W. *J. Org. Chem.* **2009**, *74*, 7743. (j) Li, F.-B.; Zhu, S.-E.; Wang, G.-W. *Chin. Sci. Bull.* **2010**, *55*, 2909. (k) Wang, G.-W.; Wang, C.-Z.; Zhu, S.-E; Murata, Y. *Chem. Commun.* **2011**, *47*, 6111. (l) Wang, G.-W.; Wang, C.-Z.; Zou, J.-P. *J. Org. Chem.* **2011**, *76*, 6088. (m) Liu, T.-X.; Li, F.-B.; Wang, G.-W. *Org. Lett.* **2011**, *13*, 6130.

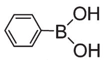
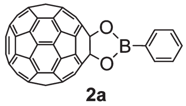
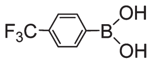
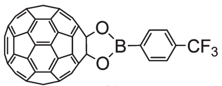
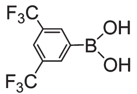
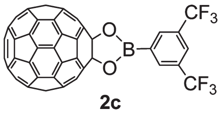
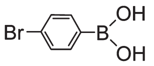
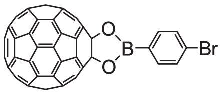
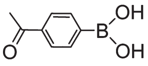
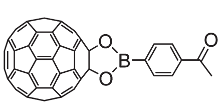
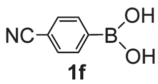
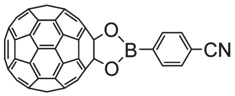
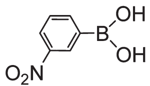
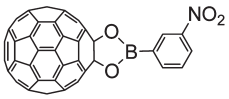
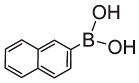
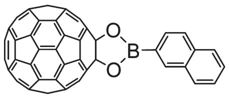
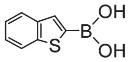
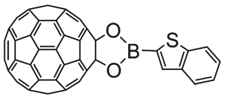
(5) For other recent examples, see: (a) Filippone, S.; Maroto, E. E.; Martín-Domenech, Á.; Suarez, M.; Martín, N. *Nat. Chem.* **2009**, *1*, 578. (b) Tzirakis, M. D.; Orfanopoulos, M. *J. Am. Chem. Soc.* **2009**, *131*, 4063. (c) Tzirakis, M. D.; Orfanopoulos, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 5891. (d) Xiao, Z.; Matsuo, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2010**, *132*, 12234. (e) Nambo, M.; Segawa, Y.; Itami, K. *J. Am. Chem. Soc.* **2011**, *133*, 2402. (f) Maroto, E. E.; de Cózar, A.; Filippone, S.; Martín-Domenech, Á.; Suarez, M.; Cossío, F. P.; Martín, N. *Angew. Chem., Int. Ed.* **2011**, *50*, 6060. (g) Lu, S.; Jin, T.; Bao, M.; Yamamoto *J. Am. Chem. Soc.* **2011**, *133*, 12842. (h) Lu, S.; Jin, T.; Kwon, E.; Bao, M.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 802.

(6) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Fagnou, K.; Lautens, M. *Chem. Rev.* **2003**, *103*, 169.

(7) (a) Li, F.-B.; Liu, T.-X.; Wang, G.-W. *J. Org. Chem.* **2008**, *73*, 6417. (b) Li, F.-B.; Liu, T.-X.; You, X.; Wang, G.-W. *Org. Lett.* **2010**, *12*, 3258. (c) Li, F.-B.; You, X.; Wang, G.-W. *Org. Lett.* **2010**, *12*, 4896.

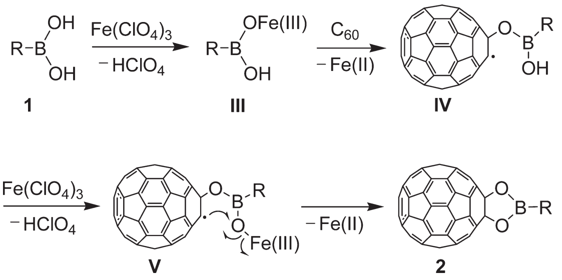
Table 1. Reaction Conditions and Yields for the $Fe(ClO_4)_3$-Mediated Reaction of C_{60} with **1a**–**i**[a]



entry	boronic acid **1**	product **2**	yield of **2** (%)[b]
1	 **1a**	 **2a**	33% (92%)
2	 **1b**	 **2b**	32% (78%)
3	 **1c**	 **2c**	38% (75%)
4	 **1d**	 **2d**	31% (69%)
5	 **1e**	 **2e**	29% (76%)
6	 **1f**	 **2f**	38% (75%)
7	 **1g**	 **2g**	28% (57%)
8	 **1h**	 **2h**	27% (93%)
9	 **1i**	 **2i**	13% (62%)

[a] All reactions were performed in a molar ratio of $C_{60}/Fe(ClO_4)_3 \cdot 6H_2O/$**1** = 1:3:5 at 100 °C for 30 min under nitrogen atmosphere. [b] Isolated yield; that in parentheses was based on consumed C_{60}.

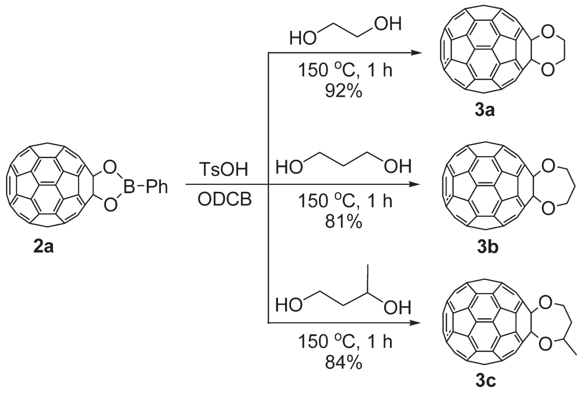
Scheme 2. Proposed Reaction Mechanism for the Formation of Fullerenyl Boronic Esters **2**



complex **V** and then intramolecular cyclization with the loss of a Fe(II) species to afford fullerenyl boronic esters **2**. Control experiments showed that **2j′** could not be obtained from the $Fe(ClO_4)_3$-mediated reaction of C_{60} with boric acid. Product **2j′** was likely formed from the spontaneous loss of the thiophene-yl group from the initially generated **2j** under our reaction conditions. The failure for the reaction with arylboronic acids bearing electron-donating groups probably arises from the lower acidity of the electron-rich arylboronic acids and alkyl boronic acids,[8] i.e., lower amount of $RB[(OH)O^-]$, retarding the formation of Fe(III) complex **III** and thus inhibiting the subsequent process. It is obvious that the mechanism for the $Fe(ClO_4)_3$-mediated formation of fullerenyl boronic esters is completely different from that for the Pd-[2d] or Rh-catalyzed[3h,i] hydroarylation of C_{60} although the same arylboronic acids were used.

The fullerenyl boronic esters are valuable precursors for further functionalization. The $ArBO_2$ moiety in products **2** was removable and used as a template to introduce other functional groups. We found that treatment of representative **2a** with ethylene glycol, 1,3-propanediol, and 1,3-butanediol in the presence of *p*-toluenesulfonic acid at 150 °C for 1 h afforded the rare C_{60}-fused dioxane/dioxepane derivatives **3a-c** in 92%, 81%, and 84% yield, respectively (Scheme 3). This transformation should proceed via the acid-catalyzed transetherization of fullerenyl boronic esters with diols.

Scheme 3. Reaction of Fullerenyl Boronic Ester **2a** with Ethylene Glycol, 1,3-Propanediol, and 1,3-Butanediol in the Presence of *p*-Toluenesulfonic Acid



Products **3a**–**c** were also fully characterized. In the ^{13}C NMR spectra of **3a** and **3b**, there were 16 lines in the range

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[8] Yan, J.; Springsteen, G.; Deeter, S.; Wang, B. *Tetrahedron* **2004**, *60*, 11205.

of 136–151 ppm for the sp^2-carbons of the C_{60} skeleton and one peak at 86–92 ppm for the sp^3-carbons of the C_{60} cage, agreeing with their C_{2v} molecular symmetry. In contrast, the ^{13}C NMR spectrum of **3c** displayed 50 lines in the 135–152 ppm range for the sp^2-carbons of the C_{60} moiety and two peaks at 91.00 and 92.66 ppm for the sp^3-carbons of the C_{60} skeleton, consistent with its C_1 molecular symmetry.

In summary, fullerenyl boronic esters have been effectively prepared by the reaction of C_{60} with boronic acids in the presence of $Fe(ClO_4)_3$ under nitrogen atmosphere, and can undergo further transformation with diols to afford novel C_{60}-fused dioxane/dioxepane derivatives. The current protocol provides facile access to fullerenyl boronic derivatives via a one-step procedure by using cheap and easily available boronic acids and $Fe(ClO_4)_3$. A possible reaction mechanism for the formation of fullerenyl boronic esters has been suggested. The study on other $Fe(ClO_4)_3$-mediated reactions of fullerenes is underway.

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Supporting Information Available. Experimental procedures, characterization data, and the ^{1}H NMR and ^{13}C NMR spectra of products **2a**–**i**, **2j′**, and **3a**–**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.