CHEMISTRY
A EUROPEAN JOURNAL

FULL PAPER

DOI: 10.1002/chem.201301617

PCy_3-Catalyzed Ring Expansion of Aziridinofullerenes with CO_2 and Aryl Isocyanates: Evidence for a Two Consecutive Nucleophilic Substitution Pathway on the Fullerene Cage

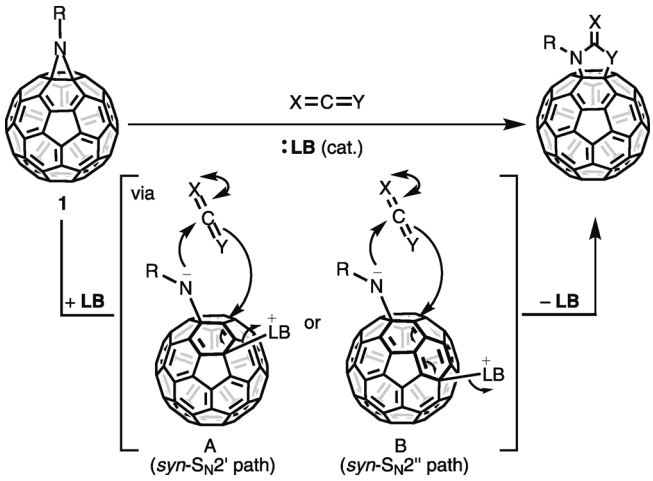
Youhei Takeda,[a, b] Hajime Kawai,[b] and Satoshi Minakata*[b]

Abstract: A PCy_3-catalyzed ring-expansion reaction of aziridine-fused fullerenes (aziridinofullerenes) through the insertion of CO_2 and aryl isocyanates is disclosed. The reaction allows for CO_2 fixation by aziridinofullerenes, producing oxazolidinone-fused fullerenes (oxazolidinofullerenes) in high yields, whereas treatment with aryl isocyanates led to a new fullerene family—imidazolidinone-fused fullerenes (imidazolidinofullerenes)—in good to high yields. Furthermore, a mechanistically related unprecedented fullerenyl phosphonium salt was successfully isolated. Using the isolated salt, mechanistic studies were also investigated.

Keywords: carbon dioxide fixation · fullerenes · Lewis bases · organocatalysis · ring expansion

Introduction

Functionalized fullerenes have been drawing much attention in the chemical community over the last few decades, because of their unique physicochemical properties. In this context, a number of distinguished organic reactions of fullerene derivatives have been developed.[1] Nevertheless, as the diversity in the reactivities and structures of functionalized fullerenes should lead to the creation of novel nanocarbon-based functional materials, further exploration and development of new reactions of fullerenes and their derivatives still remain a challenge. Herein we present a PCy_3-catalyzed ring-expansion reaction of aziridinofullerenes **1** with CO_2 and aryl ioscyanates through a two-consecutive nucleophilic substitution pathway (S_N2' or S_N2'' mechanism), giving five-membered heterocycle-fused fullerene derivatives that are otherwise difficult to access efficiently by conventional methods or constitute a new class of fullerene derivatives (Scheme 1).



Scheme 1. LB-catalyzed ring-expansion of aziridinofullerenes **1** with heterocumulenes.

The concept of "Lewis base (LB) catalysis" has been emerging as a powerful strategy for realizing diverse organic synthetic reactions, such as the Morita–Baylis–Hillman and Rauhut–Currier reactions, owing to the capability of LBs to activate a wide variety of reagents and substrates (nucleophiles, electrophiles, and ambiphilic reagents) through flexible molecular interactions, such as n–π*, n–σ*, and n–n*.[2] However, contrary to its diversity in common organic reactions, LB-catalyzed reactions of fullerene derivatives have been much less explored, whereas the Lewis acid (LA)-catalyzed counterparts have been well-documented.[3] Representative examples of such LB catalysis involve: 1) tertiary phosphine (PR_3)-catalyzed [3+2] cycloaddition of C_{60} with Michael-acceptors, such as buta-2,3-dienoates[4a,b] and but-2-ynoates[4a] to give carbocycle-fused fullerenes, 2) chloramine salts-catalyzed rearrangement of [6,6]-closed aziridinofullerenes to [5,6]-opened azafulleroids,[5] and 3) tertiary amine-induced ring-closure of fullerene chlorohydrins to give epoxy fullerenes.[6] The major impediment in developing LB-catalyzed reactions of fullerene derivatives would be the intrinsic high affinities toward LBs,[7] such as amines and phosphines, leading to the deactivation of LB catalysts. For example, the treatment of primary and secondary amines,

[a] Dr. Y. Takeda
Frontier Research Base for Global Young Researchers
Graduate School of Engineering, Osaka University
Yamadaoka 2-1, Suita, Osaka 565-0871 (Japan)

[b] Dr. Y. Takeda, H. Kawai, Prof. Dr. S. Minakata
Department of Applied Chemistry, Graduate School of Engineering
Osaka University, Yamadaoka 2-1, Suita, Osaka 565-0871 (Japan)
E-mail: minakata@chem.eng.osaka-u.ac.jp

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201301617.

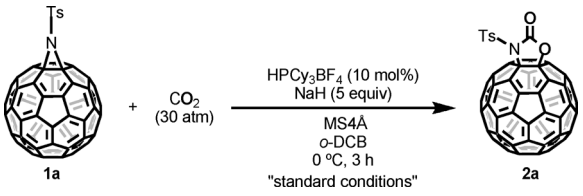
such as *n*-$PrNH_2$ and ethylenediamine, results in the irreversible formation of multi-adducts, $C_{60}H_n(NRR')_n$ (predominantly $n=6$).[8] During the course of our studies on developing novel synthetic methods of heterocycle-fused fullerenes,[9] it occurred to us that ring-expansion of aziridine-fused fullerenes **1** by the insertion of heterocumulenes, like CO_2, would be a diverse approach to five-membered heterocycle-fused fullerenes that are otherwise difficult to synthesize directly from C_{60} (Scheme 1). Although LB-catalyzed ring-expansion reactions of "normal aziridines", which are not fused with the fullerene cage, with heterocumulenes through double S_N2 processes have been extensively studied,[10] the ring-expansion of **1** has not yet been realized, due to the infeasibility of back-side attack of the aziridine carbons by LB catalyst. We assumed that an appropriate LB would facilitate the nucleophilic ring-opening of **1** in a *syn*-S_N2' or S_N2'' fashion on the fullerene cage[11] to generate zwitterion **A** or **B**, respectively, driven by the release of its high strain of the aziridine ring (Scheme 1).[12] Given that the resulting nitrogen anion captures heterocumulenes followed by kick-back attack on the fullerene carbons, ring-expanded product would be formed with regeneration of LB catalyst.

Results and Discussion

To verify our assumption, we chose *N*-toluenesulfonyl aziridinofullerene (**1a**) as a fullerene substrate and CO_2 as a heterocumulene (Table 1). As a result of extensive screening of reaction conditions, such as LBs, solvents, temperatures, and CO_2 pressures,[13] we were delighted to find that the desired reaction proceeded efficiently under pressurized CO_2 (30 atm) at 0 °C in the presence of 10 mol % of tricyclohexylphosphine (PCy_3), which was in situ generated from its salt $HPCy_3BF_4$ and NaH, to give oxazolidinofullerene (**2a**)[14] in as high as 86 % yield ("standard conditions"). The use of phosphine as the salt $HPCy_3BF_4$ instead of PCy_3 was found to be significantly important in terms of chemical yield of **2a** (entry 1 vs. 2). Intriguingly, the counter ions (Na^+ and $^-BF_4$) also play a pivotal role for efficient progression of the reaction, although the detailed function is unclear at present (entry 3). It should be noted that the ring-expansion was specific to PCy_3 ($pK_a=9.7$).[15] Although a variety of tertiary phosphines and their HBF_4 salts were employed as a catalyst, **2a** was not produced at all (entries 4–7), whereas tricyclopentylphosphine ($PCyp_3$) gave **2a** in significantly low yield (entry 8). In some cases, small amounts of C_{60} were produced. Amines, such as DABCO, DMAP, Et_3N, and pyridine, were ineffective for the reaction. A representative *N*-heterocyclic carbene (NHC), IPr, which reportedly adds to C_{60} to give the stable fullerene LA–LB adduct,[16] also failed to produce **2a**. Inorganic LBs, such as LiI and LiBr, which serve as catalysts in the ring-expansion of "normal aziridines",[10] did not work with this aziridine substrate. Regarding factors other than LBs, the pressurized CO_2 was required to gain product in high yield, suggesting the existence of equilibrium in this system (entries 9 and 10). It is worth noting that both deaerated *o*-dichlorobenzene (*o*-DCB) as solvent and MS4 Å as a dehydrating agent were necessary to gain high yield of **2a**, probably because of the lability of PCy_3 to oxygen and moisture.

With the optimized conditions in hand, the substrate scope of **1** was investigated (Table 2). Although an electronically neutral substituent (Ph, **1b**) did not affect the efficiency (entry 1), the reaction with aziridinofullerene bearing a strong electron-withdrawing group (*p*-NO_2, **1c**) was significantly retarded and resulted in low yield of **2c** (entry 2), probably due to the lower nucleophilic nature of the intermediately resulting carboxylate anion. On the other hand, substrates with an electron-donating group (*p*-$MeOC_6H_4$, Me) afforded the corresponding products **2d** and **2e**, respec-

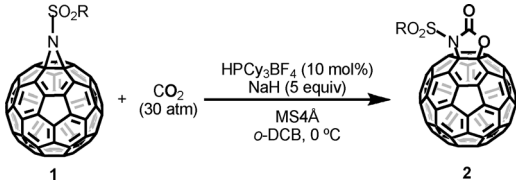
Table 1. Summary of optimization studies of PCy_3-catalyzed ring-expansion of **1a** with CO_2.[a]



Entry	Changes from "standard conditions"	Yield of **2a** [%]	Recovery of **1a** [%]
1	none	86	8
2	PCy_3[b]	24	8
3	PCy_3[b] + $NaBF_4$	45	16
4	PPh_3 (pK_a 2.3)[c]	0	100
5	$HPMe_3BF_4$ (pK_a 8.6)[c]	0	81
6	$HP(tBu)_3BF_4$ (pK_a 11.4)[c]	0	100
7	$HP(tBu)_2MeBF_4$	0	100
8	$HPCyp_3BF_4$	12	75
9	under 1 atm of CO_2	0	94
10	under 5 atm of CO_2	21	74

[a] Reaction conditions: **1a** (25 μmol), $HPCy_3BF_4$ (2.5 μmol), NaH (125 μmol), and MS4 Å (10 mg) in deaerated *o*-DCB (1.5 mL) under pressurized CO_2 atmosphere (30 atm) at 0 °C for 3 h. [b] A 0.66 M toluene solution was used. [c] See ref. [15].

Table 2. Scope of **1** in the ring-expansion reaction.[a]



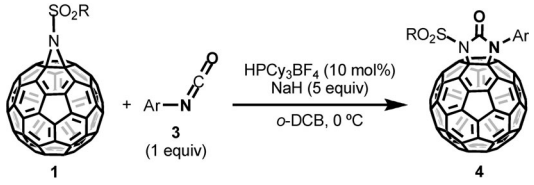
Entry	R (**1**)	*t* [h]	**2a**	Yield [%]	Recovery of **1** [%]
1	Ph (**1b**)	3	**2b**	85	15
2	*p*-NO_2-C_6H_4 (**1c**)	15	**2c**	23	65
3	*p*-MeO-C_6H_4 (**1d**)	24	**2d**	70	2
4	Me (**1e**)	24	**2e**	70	trace

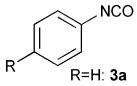
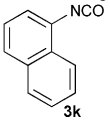
[a] Reaction conditions: **1** (25 μmol), $HPCy_3BF_4$ (2.5 μmol), NaH (125 μmol), and MS4 Å (10 mg) in deaerated *o*-DCB (1.5 mL) under pressurized CO_2 (30 atm) at 0 °C for the time indicated.

tively, in good yields, albeit prolonged time (entries 3 and 4). Conventional methods for preparing **2** involve LA (BBr_3 or TMSCl)-mediated rearrangement of *N*-ethoxycarbonyl aziridinofullerenes and hydrolysis of the rearranged intermediates.[14] In light of the fact that these conventional methods require excess amounts of LAs, and that the substrate scope is limited, our method is more efficient and versatile than precedents.

Having established ring-expansion with CO_2, we then turned our attention to widening the scope of heterocumulene substrates. Among the heterocumulenes attempted, aryl isocyanates **3** were found to serve as good electrophiles for LB-catalyzed ring-expansion of **1** (Table 3).[17] As a

Table 3. PCy_3-catalyzed ring-expansion of **1** with **3**.[a]

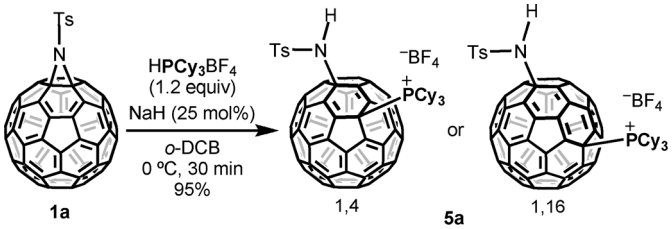


Entry	R (**1**)	**3**	*t* [h]	**4**	Yield [%]
1	*p*-MeC_6H_4 (**1a**)	 R=H: **3a**	24	**4aa**	68
2	**1a**	R = *n*Bu: **3b**	24	**4ab**	62
3	**1a**	R = OMe: **3c**	48	**4ac**	70
4	**1a**	R = F: **3d**	24	**4ad**	73
5	**1a**	R = Cl: **3e**	18	**4ae**	83
6	**1a**	R = Br: **3f**	24	**4af**	71
7	**1a**	R = I: **3g**	48	**4ag**	78
8	**1a**	R = CO_2Et: **3h**	15	**4ah**	74
9	**1a**	 R=Cl: **3i**	24	**4ai**	71
10	**1a**	R = NO_2: **3j**	42	**4aj**	62
11	**1a**	 **3k**	24	**4ak**	86
12	Ph (**1b**)	**3k**	15	**4bk**	75
13	*p*-$NO_2C_6H_4$ (**1c**)	**3k**	12	**4ck**	92
14	*p*-$MeOC_6H_4$ (**1d**)	**3k**	15	**4dk**	78
15	Me (**1e**)	**3k**	15	**4ek**	64
16	*o*-$NO_2C_6H_4$ (**1f**)	**3k**	15	**4fk**	91
17	*p*-BrC_6H_4 (**1g**)	**3k**	15	**4gk**	65

[a] Reaction conditions: **1** (25 μmol), **3** (25 μmol), $HPCy_3BF_4$ (2.5 μmol), and NaH (125 μmol) in deaerated *o*-DCB (1.5 mL) at 0 °C for the time indicated.

result of the modification study of reaction conditions,[13] it was revealed that the ring-expansion of **1a** proceeded smoothly even with an equimolar amount of phenyl isocyanate (**3a**) to produce unsymmetrical imidazolidinone-fused fullerene **4aa** in 68% yield (entry 1).[18] Under the optimized conditions, a wide variety of imidazolidinofullerenes bearing an alkyl- (**4ab**), alkoxy- (**4ac**), halogeno- (**4ad**, **4ae**, **4af**, and **4ag**), and ester (**4ah**) substituent at the *p*-position of the Ar moiety were successfully produced in good to high yields without any loss of their functionalities (entry 2–8). An *o*-substituent did not affect product yields (entries 9 and 10). Sterically demanding isocyanate **3k** also served as a good substrate to produce **4ak** in high yield (entry 11). Aziridinofullerenes bearing various *N*-substituents **1b**–**1g** were also efficiently converted into products **4bk**–**4gk** with high functional compatibility (entries 12–17). It is noted that these fullerene derivatives constitute a new class of fullerene family.

During the attempt at obtaining mechanistic insights, we succeeded in isolating unprecedented fullerenyl phosphonium salt **5a**, which is closely associated with zwitterion **A** and **B**, by the stoichiometric treatment of **1a** with $HPCy_3BF_4$ in the presence of catalytic amount of NaH (Scheme 2). Notably, the salt **5a** was stable enough to toler-

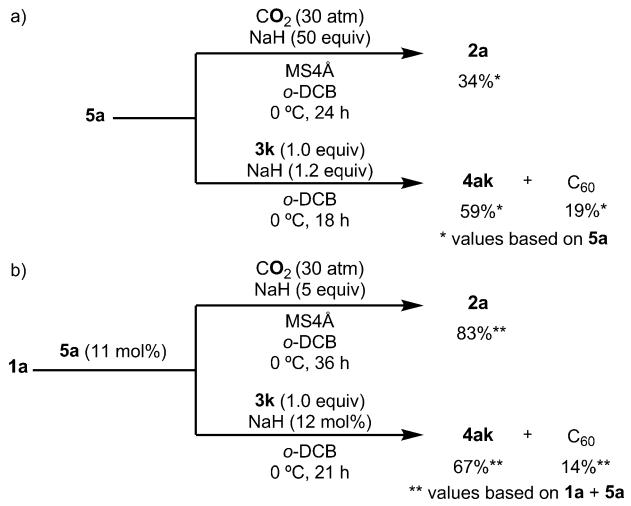


^{1}H NMR: δ=8.09 ppm (H/D exchangeable)
^{13}C NMR: 58 signals in δ=120–150 ppm
^{31}P NMR: δ=40.2 ppm

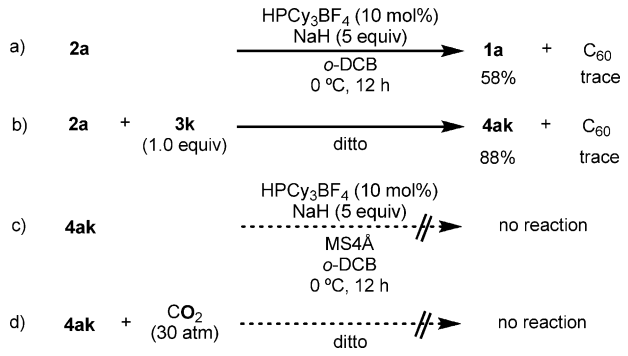
Scheme 2. Preparation and isolation of fullerenyl salt **5a**.

ate the purification with silica gel column chromatography. The salt was characterized by MS, NMR and IR spectroscopy.[13] The broad singlet ^{1}H NMR (*o*-DCB-d_4) peak at δ = 8.09 ppm underwent smooth H/D exchange upon D_2O addition, indicating the existence of N–H. Two distinct ^{13}C NMR resonances at δ = 56.3 and 63.0 ppm coupled with ^{31}P nucleus ($J_{C\text{-}P}$ = 37.8 and 3.5 Hz, respectively) and confirmed the presence of two sp^3-hybridized fullerene carbons connected to NHTs and PCy_3. More importantly, the 58 ^{13}C NMR resonances in the sp^2-hybridized fullerene regime (δ = 120–150 ppm) assured the unsymmetrical 1,4- or 1,16-substitution pattern (Scheme 2).[19,20] This undoubtedly provides evidence for the occurrence of the nucleophilic substitution event on the fullerene cage (S_N2' or S_N2''), which has been only proven by the hydrolysis of fluorofullerenes.[11] Furthermore, to the best of our knowledge, this is the first example of the isolation and characterization of tetravalent fullerenyl phosphonium salt.[21]

To gain insights into the species involved in the catalytic reaction, stoichiometric and catalytic reactions of **5a** were performed (Scheme 3). The stoichiometric reactions of **5a** with CO_2 and isocyanate **3k** under the "standard conditions" produced ring-expanded products **2a** and **4ak**, respectively, in moderate yields with slight formation of C_{60} (Scheme 3a). Catalytic reactions also gave the same ring-expand-



Scheme 3. Mechanistic studies with **5a**: a) stoichiometric experiments, b) catalytic experiments.

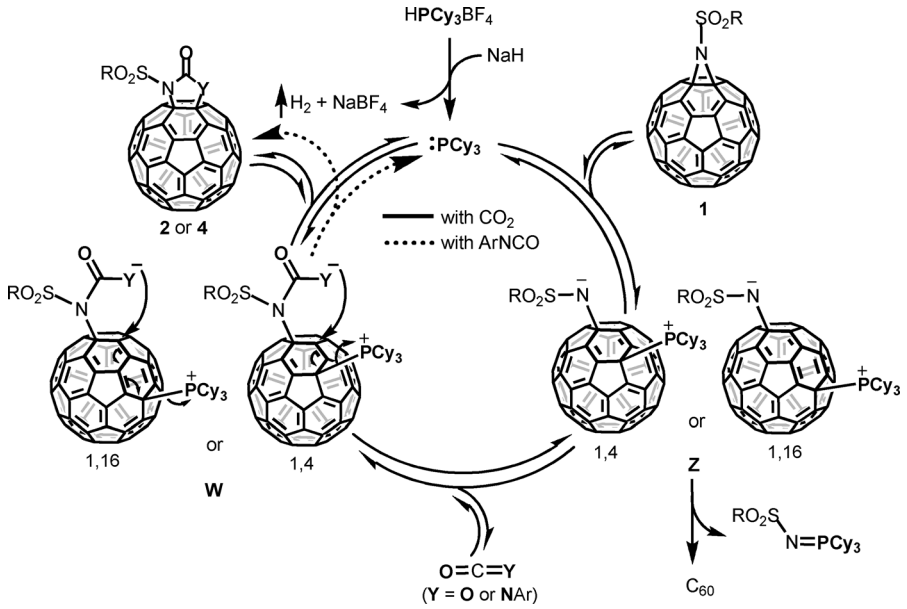


Scheme 4. Reversibility tests.

ed products in high yield (Scheme 3b), suggesting that the zwitterion (**A** or **B** in Scheme 1; R = Ts, LB = PCy_3) generated by the N–H abstraction of **5a** would be the catalytically active species as we preliminarily assumed.

To check the reaction reversibility, we subjected ring-expanded products **2a** and **4ak** separately to the "standard conditions" in the absence and presence of heterocumulenes (Scheme 4). Oxazolidinofullerene **2a** underwent decarboxylation in both cases, affording aziridinofullerene **1a** (Scheme 4a) and heterocumulene-switched product **4ak** (Scheme 4c). These results indicate that all the elementary steps in the ring-expansion with CO_2 are reversible, in agreement with the fact that the employment of pressurized CO_2 conditions was required to obtain product **2** in high yields. In sharp contrast, **4ak** did not change at all either in the absence or presence of CO_2 (Scheme 4c and d), indicating the irreversibility of the product formation step.

Taken together, a plausible catalytic cycle is shown in Scheme 5. The S_N2' or S_N2'' ring-opening of **1** with PCy_3 would generate zwitterion **Z**, and the capture of heterocumulenes with the resulting RO_2SN^- (**W**) followed by the ring-closure through the second S_N2' or S_N2'' event should give ring-expanded products. C_{60} could be formed through the elimination of iminophosphorane $RO_2SN{=}PCy_3$ from zwitterion **Z**.[22]



Scheme 5. Plausible catalytic cycle.

Conclusion

In conclusion, we have developed an efficient and versatile ring-expansion of aziridinofullerenes with CO_2 and aryl isocyanates with the aid of LB catalysis. The reaction allowed the synthesis of a series of five-membered heterocycle-fused fullerenes. Furthermore, a mechanistically related fullerenyl phosphonium salt was isolated and characterized, which offered discrete evidence for the nucleophilic substitution event (S_N2' or S_N2'') on the fullerene cage. Investigation on the precise mechanism and the physicochemical properties of the new fullerene family are underway in our laboratory.

Experimental Section

Typical procedure for the ring-expansion of 1 with CO_2: Aziridinofullerene **1** (25 μmol), $HPCy_3BF_4$ (0.9 mg, 2.5 μmol), MS4 Å (10 mg) and deaerated *o*-DCB (1.5 mL) were placed in a 20 mL stainless-steel autoclave. After being stirred for 5 min at room temperature, NaH (60%, disper-

sion in paraffin liquid, 5.0 mg, 0.125 mmol) was added to the solution, and then the vessel was charged with CO_2 (30 atm). The resulting mixture was allowed to stir at 0 °C for the indicated time in Tables 1 and 2. After the completion of the reaction, the mixture was passed through a short column on a silica gel pad (3 g), and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using toluene as an eluent.

Compound data for a representative oxazolidinofullerene, 2a: Black crystalline solid; $R_f = 0.16$ (1:1 toluene/hexane); ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 2.54$ (s, 3H), 7.47 (d, 2H, $J = 8.1$ Hz), 8.17 ppm (d, 2H, $J = 8.1$ Hz); ^{13}C NMR (150 MHz, 1:1 $CDCl_3/CS_2$) $\delta = 21.9$, 77.8, 93.8, 129.2, 129.8, 134.7, 136.8, 137.1, 138.7, 140.1, 141.0, 141.4, 141.8, 142.3 (2C), 142.5, 142.6, 142.8, 142.9, 143.3, 143.5, 143.8, 144.5 (2C), 145.22 (2C), 145.29, 146.1, 146.2, 146.3, 146.4 (2C), 146.4, 146.62, 146.66, 148.2, 148.3, 150.8 ppm; FTIR (KBr): $\tilde{\nu} = 3450$, 2919, 1793, 1384, 1083 cm^{-1}; MS (FAB): m/z 933 $[M]^+$; HRMS (FAB): m/z calcd for $C_{68}H_7NO_4S$: 933.0096 $[M]^+$; found: 933.0115.

Typical procedure for the ring-expansion of 1 with 3: Aziridinofullerene **1** (25 μmol), $HPCy_3BF_4$ (0.9 mg, 2.5 μmol), and deaerated *o*-DCB (1.5 mL) were placed in a 10 mL Schlenk flask. After being stirred for 5 min at room temperature, aryl isocyanate **3** (25 μmol) and NaH (60%, dispersion in paraffin liquid, 5.0 mg, 0.125 mmol) were added to the solution. The resulting mixture was allowed to stir at 0 °C for the time indicated in Table 3. After the completion of the reaction, the mixture was passed through a short column on a silica gel pad (3 g), and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: 95:5 toluene/AcOEt).

Compound data for a representative imidazolidinofullerene, 4aa: Brown solid; $R_f = 0.48$ (95:5 toluene/AcOEt); ^{1}H NMR (270 MHz, $CDCl_3$): $\delta =$ 2.51 (s, 3H), 7.43 (d, 2H, $J = 8.1$ Hz), 7.45–7.52 (m, 3H), 7.66 (d, 2H, $J =$ 8.5 Hz), 8.19 ppm (d, 2H, $J = 8.5$ Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta =$ 29.6, 79.2, 81.5, 128.9, 129.1, 129.6, 129.7, 130.7, 130.9, 134.2, 136.2, 136.6, 138.4, 139.7, 141.4, 141.5, 141.9, 142.0, 142.1, 142.7, 142.81, 142.85, 142.9, 144.0, 144.4, 144.66, 144.67, 145.1, 145.20, 145.26, 145.4, 145.6, 146.0, 146.2, 146.41, 146.42, 146.61, 146.63, 146.68, 148.0, 148.1, 152.3 ppm; FTIR (KBr): $\tilde{\nu} = 3423$, 2923, 1742, 1654, 1629, 1164, 1072 cm^{-1}; MS (FAB): m/z 1008 $[M]^+$; HRMS (FAB): m/z calcd for $C_{74}H_{12}N_2O_3S$: 1008.0569 $[M]^+$; found: 1008.0556.

Acknowledgements

This research was partly supported by a Grant-in-Aid for Scientific Research on Innovative Areas "Molecular Activation Directed toward Straightforward Synthesis" from the MEXT, Japan. Y.T. acknowledges support from the Frontier Research Base for Global Young Researchers, Osaka University, on the Program of MEXT.

[1] a) A. Hirsch, M. Brettreich, *Fullerenes: Chemistry and Reactions*, Wiley-VCH, Weinheim, Germany, **2005**; b) *Fullerenes: Chemistry, Physics, and Technology* (Eds.: K. M. Kadish, R. S. Ruoff), Wiley, New York, **2000**; c) K. Itami, *Chem. Rec.* **2011**, *11*, 226; d) Y. Matsuo, E. Nakamura, *Chem. Rev.* **2008**, *108*, 3016; e) N. Martín, M. Altable, S. Filippone, A. Martín-Domenech, *Synlett* **2007**, 3077; f) N. Martín, *Chem. Commun.* **2006**, 2093.

[2] S. Denmark, G. Beutner, *Angew. Chem.* **2008**, *120*, 1584; *Angew. Chem. Int. Ed.* **2008**, *47*, 1560.

[3] Selected examples: a) Y. Tajima, K. Takeshi, Y. Shigemitsu, Y. Numata, *Molecules* **2012**, *17*, 6395; b) Z. Jiang, Y. Zhang, L. Gan, Z. Wang, *Tetrahedron* **2008**, *64*, 11394; c) G. A. Olah, I. Bucsi, D. S. Ha, R. Aniszfeld, C. S. Lee, G. K. S. Prakash, *Full. Sci. Technol.* **1997**, *5*, 389; d) G. A. Olah, I. Bucsi, R. Aniszfeld, G. K. S. Prakash, *Carbon* **1992**, *30*, 1203; e) G. A. Olah, I. Bucsi, C. Lambert, R. A. Aniszfeld, N. J. Trivedi, D. K. Sensharma, G. K. S. Prakash, *J. Am. Chem. Soc.* **1991**, *113*, 9387; f) G. A. Olah, I. Bucsi, C. Lambert, R. Aniszfeld, N. J. Trivedi, D. K. Sensharma, G. K. S. Prakash, *J. Am. Chem. Soc.* **1991**, *113*, 9385.

[4] a) B. F. O'Donovan, P. B. Hitchcock, M. F. Meidine, H. W. Kroto, R. Taylor, D. R. M. Walton, *Chem. Commun.* **1997**, 81; b) L.-H. Shu, W.-Q. Sun, D.-W. Zhang, S.-H. Wu, H.-M. Wu, J.-F. Xu, X.-F. Lao, *Chem. Commun.* **1997**, 79.

[5] a) R. Tsuruoka, T. Nagamachi, Y. Murakami, M. Komatsu, S. Minakata, *J. Org. Chem.* **2009**, *74*, 1691; b) S. Minakata, R. Tsuruoka, T. Nagamachi, M. Komatsu, *Chem. Commun.* **2007**, 323.

[6] Z. Jia, X. Zhang, G. Zhang, S. Huang, H. Fang, X. Hu, Y. Li, L. Gan, S. Zhang, D. Zhu, *Chem. Asian J.* **2007**, *2*, 290.

[7] Chapter 3 of ref. [1a] details the reactivities of C_{60} toward LBs.

[8] A. Hirsch, Q. Li, F. Wudl, *Angew. Chem.* **1991**, *103*, 1339; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1309.

[9] a) Y. Takeda, S. Enokijima, T. Nagamachi, K. Nakayama, S. Minakata, *Asian J. Org. Chem.* **2013**, *2*, 91; b) T. Nagamachi, Y. Takeda, K. Nakayama, S. Minakata, *Chem. Eur. J.* **2012**, *18*, 12035.

[10] a) Z.-Z. Yang, L.-N. He, J. Gao, A.-H. Liu, B. Yu, *Energy Environ. Sci.* **2012**, *5*, 6602; b) T. Sakakura, J.-C. Choi, H. Yasuda, *Chem. Rev.* **2007**, *107*, 2365.

[11] Only a few examples of proven S_N2' and S_N2'' reactions on the fullerene cage have been reported, see: a) B. W. Clare, D. L. Kepert, R. Taylor, *Org. Biomol. Chem.* **2003**, *1*, 3618; b) A. G. Avent, A. K. Abdul-Sada, B. W. Clare, D. L. Kepert, J. M. Street, R. Taylor, *Org. Biomol. Chem.* **2003**, *1*, 1026.

[12] Recently, Itami and co-workers reported Brønsted acid (TfOH)-catalyzed S_N1-type multi-arylation of **1**: M. Nambo, Y. Segawa, K. Itami, *J. Am. Chem. Soc.* **2011**, *133*, 2402.

[13] For details, see the Supporting Information.

[14] The spectroscopic data of **2a** were consistent with those previously reported in the literatures: a) M. R. Banks, J. L. C. Cadogan, I. Gosney, P. K. G. Hodgson, P. R. R. Langridge-Smith, J. R. A. Millar, A. T. Taylor, *Tetrahedron Lett.* **1994**, *35*, 9067; b) L.-L. Shiu, K.-M. Chien, T.-Y. Liu, T.-I. Lin, G.-R. Her, S.-L. Huang, T.-Y. Luh, *J. Chem. Soc. Perkin Trans. 1* **1994**, 3355.

[15] W. A. Henderson, C. A. Streuli, *J. Am. Chem. Soc.* **1960**, *82*, 5791.

[16] H. Li, C. Risko, J. H. Seo, C. Campbell, G. Wu, J.-L. Brédas, G. C. Bazan, *J. Am. Chem. Soc.* **2011**, *133*, 12410.

[17] Attempts at ring-expansion with other heterocumulenes, such as CS_2, RN=C=S, RN=C=Se, ArCN, and RN=C=NR failed.

[18] The chemical structure of product **4** was characterized with ^{1}H and ^{13}C NMR spectroscopy, IR, and mass spectroscopy. For details, see the Supporting Information.

[19] If **5a** had a 1,2-pattern, 32 ^{13}C NMR signals would have been observed in the sp^2-hybridized fullerene regime.

[20] Although we tried to make a single crystal suitable for the X-ray structural analysis, it failed. From the data in hand it would be difficult to determine whether the structure of **5a** is 1,4- or 1,16-substitution pattern. Addition of tris(trimethylsilyl)lithium to C_{60} reportedly gives bis-adduct with 1,16-pattern: T. Kusukawa, W. Ando, *Angew. Chem.* **1996**, *108*, 1416; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1315.

[21] Preparation of tri- and pentavalent fullerenyl phosphines have been reported: a) H. Isobe, A.-J. Chen, N. Solin, E. Nakamura, *Org. Lett.* **2005**, *7*, 5633; b) S.-H. Wu, W.-Q. Sun, D.-W. Zhang, L.-H. Shu, H.-M. Wu, J.-F. Xu, X.-F. Lao, *Tetrahedron Lett.* **1998**, *39*, 9233; c) S. Yamago, M. Yanagawa, H. Mukai, E. Nakamura, *Tetrahedron* **1996**, *52*, 5091; d) S. Yamago, M. Yanagawa, E. Nakamura, *J. Chem. Soc. Chem. Commun.* **1994**, 2093.

[22] The production of $TsN=PCy_3$ was confirmed by ^{1}H NMR spectroscopy in the monitoring of the treatment of salt **5a** with NaH.

Received: April 27, 2013
Published online: August 16, 2013

