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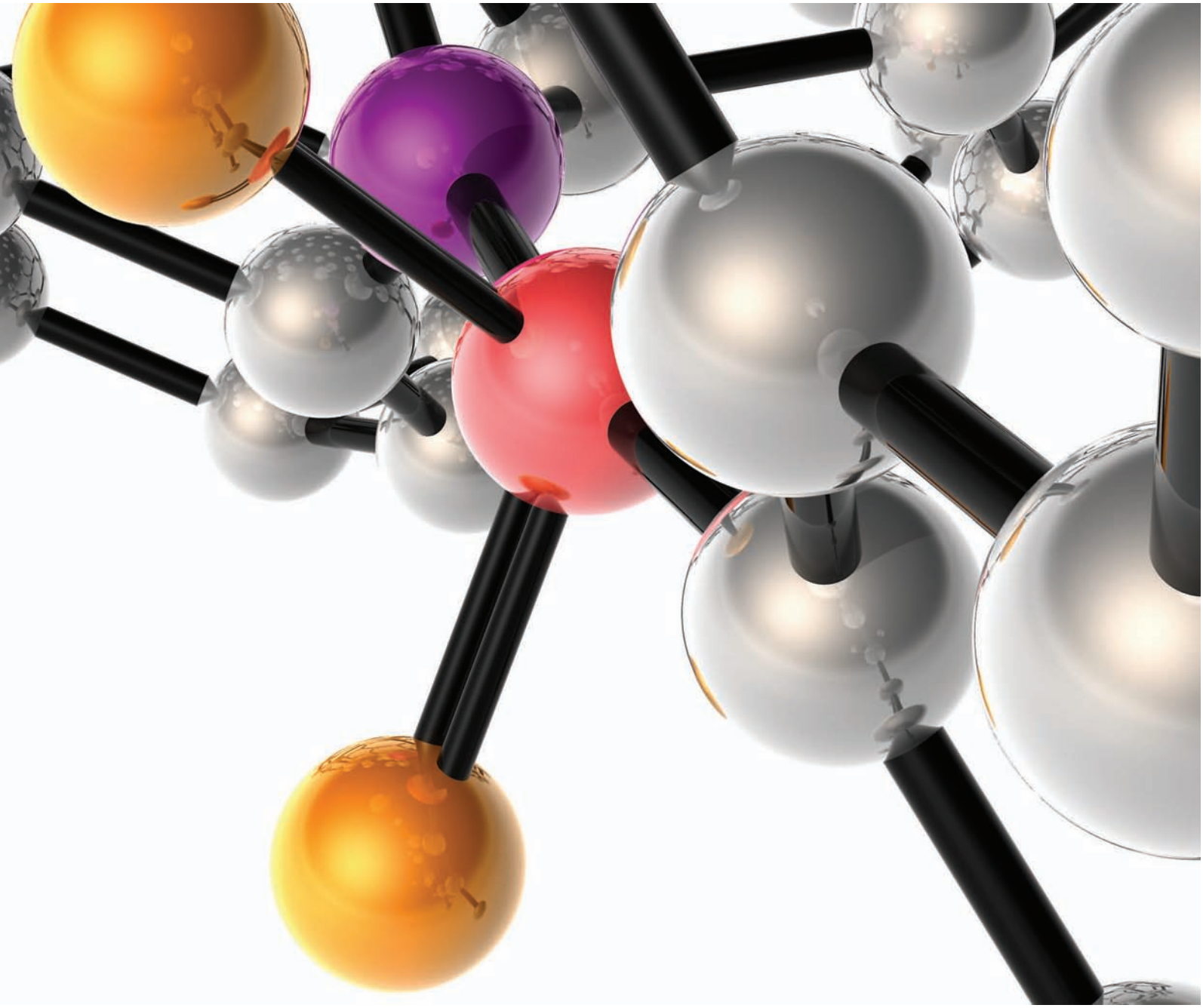

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The ionic introduction of an N_1 unit to C_{60} and a unique rearrangement of aziridinofullerene†

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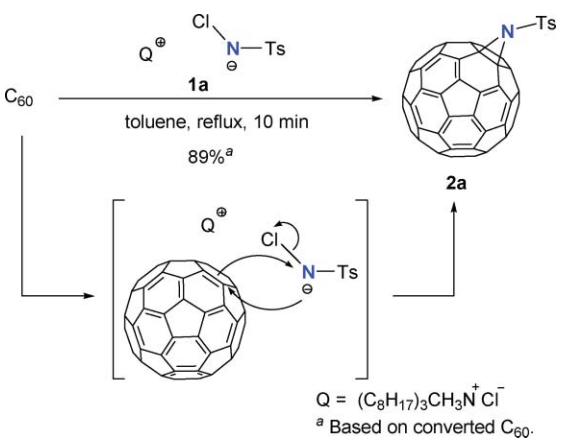
A new chloramine-based aziridination of C_{60} and unique rearrangement of aziridinofullerene to azafulleroid is described. The ionic introduction of an N_1 unit to C_{60} *via* an addition–cyclization mechanism was first achieved under mild conditions; the combination of chloramine and MS4A resulted in the promising rearrangement of aziridinofullerene to azafulleroid, and the isomerization could be performed catalytically.

The development of a basic and facile method for the functionalization of C_{60} remains an important challenge because of recent demands for carbon nanomaterials.[1] The introduction of N_1 units to C_{60} with organic azides, leading to closed [6,6]-bridged aziridinofullerenes[2] and opened [5,6]-bridged azafulleroids,[3] was originally developed by Wudl *et al.*[3a] Since then, other examples of aziridination using nitrenes[4,5] or an iminoiodane under ultrasonic irradiation[6] have been reported. Aziridinofullerenes and azafulleroids are commonly formed *via* 1,3-dipolar cycloaddition, by the addition of nitrenes, or through radical reactions. Isomerization of the two compounds is performed by thermal treatment[7] or photoirradiation.[3b,8] Selective formation of the two isomers, involving N_2 extrusion from triazorinofullerenes, can be controlled by thermal or photochemical conditions.[8a] The aziridination of C_{60} is a powerful method for rendering the molecule functional; azafulleroids, in particular, are key precursors for azafullerene "$C_{59}N$" synthesis.[9] However, some problems remain—namely, most nitrogen sources are not commercially available and require careful handling. Alternatively, our group has developed methods for the aziridination of olefins[10] using chloramine-T (CT) as an N_1 source; however, these methods are ineffective for the formation of aziridinofullerenes. This paper describes the first example of the ionic aziridination of C_{60} with chloramines utilizing the electron-acceptor nature of C_{60} *via* nucleophilic addition followed by intramolecular cyclization. Addition of molecular sieves, 4A (MS4A) to the reaction system induced the unique rearrangement of aziridinofullerene to azafulleroid.

CT was first converted into its ammonium salt because of its low solubility in toluene. The reaction of C_{60} with an equimolar amount of ion-exchanged CT, **1a**, in toluene under reflux for 10 min gave closed, [6,6]-bridged *N*-4-methylbenzenesulfonyl-azirizinofullerene (**2a**) in 89% yield (Scheme 1). Increasing the reaction time caused the formation of multi-CT adducts, leading to a decrease in the yield of the monoadduct. Even though the reaction proceeded at ambient temperature, the efficiency was rather low compared to reflux conditions. The recovered and reusable C_{60} (81%) was easily separable by silica gel column chromatography. Two possible pathways—addition of a nitrene species generated by the dechlorination of chloramine **1a** or the ionic addition–cyclization path shown in Scheme 1—should be considered for the present aziridination of C_{60}. Because it is known that a triplet nitrene is generated from CT and $AgNO_3$,[10d] the system was employed in this reaction with C_{60}, but no adduct was formed. Although nitrene should not be generated from CT in the absence of $AgNO_3$, the treatment of C_{60} with **1a** under an atmosphere of oxygen gave the same result as that shown in Scheme 1, indicating that the reaction did not involve radical species. Moreover, the desired aziridinofullerene was not produced at all in the water–toluene bilayer system. From these experiments, the active species of the present reaction must be the anionic nitrogen of CT. Therefore, the aziridination can be regarded as an aza-version of the Bingel reaction.[11]

When optimizing the reaction conditions, the addition of MS4A to the reaction system not only improved the efficiency of the reaction but also produced opened, [5,6]-bridged azafulleroid **3a** as a main product (Table 1, entry 1 *vs.* 2). Since aziridinofullerene **2a** rearranged at 180 °C in *ortho*-dichlorobenzene for 5 h to give **3a** in 58% yield, the effect of MS4A on the formation of **3a** was readily apparent. The result indicates that azafulleroid **3a** was formed under thermodynamic control and aziridinofullerene **2a** was selectively formed under kinetic control in the relatively mild conditions.

The addition of $CaCl_2$ in place of MS4A did not result in the formation of any azafulleroid **3a**, suggesting that MS4A does not



Scheme 1 Addition–cyclization of CT to C_{60}.

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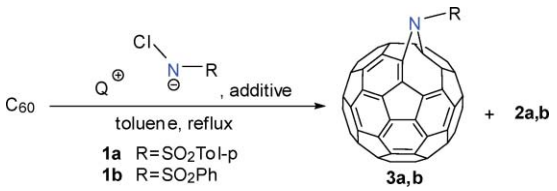
Table 1 Effects of MS4A on the formation of azafulleroids



Entry	Chloramine (equivalents)	Additive	Time/min	Yield (%)[a,b]	Ratio (**3**/**2**)
1	**1a** (1.0)	None	10	89 (17)	0/100
2	**1a** (1.0)	MS4A	10	90 (27)	63/37
3	**1a** (1.0)	Alumina (neutral)	10	44 (16)	56/64
4	**1a** (1.0)	Alumina (basic)	10	59 (16)	69/31
5	**1a** (1.0)	$^{n}Pr_3N$	10	61 (11)	55/45
6	**1a** (1.0)[c]	MS4A	10	32 (9)	86/14
7	**1b** (1.0)	MS4A	5	89 (19)	26/74
8	**1b** (1.6)	MS4A	15	55 (4)	100/0

[a] Total yields of **2** and **3** based on converted C_{60}. [b] The number in parentheses is the isolated yield. [c] CT and MS4A were mixed in Et_2O before being added to the toluene solution of C_{60}.

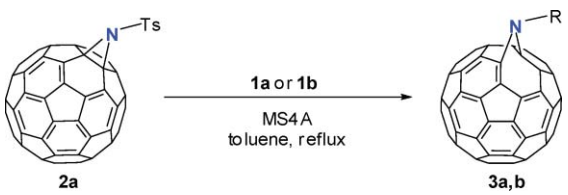
act as a dehydrating agent. Basic alumina was more effective than neutral alumina for the formation of **3a** (Table 1, entries 3 and 4). As well as **2a**, fulleroid **3a** was also yielded by the use of tripropyl amine (Table 1, entry 5). From these results, the basicity and the interaction between MS4A and chloramine **1a** are important for the formation of the azafulleroid. To enhance the interaction, MS4A was mixed with **1a** in diethyl ether, followed by removal of the solvent. Next, the composite was treated with fullerene under the same conditions to predominately yield the azafulleroid, as expected (Table 1, entry 6). Ion-exchanged **1b**, derived from another commercially available chloramine-B, also effectively introduced an N_1 unit to C_{60} (Table 1, entry 7), and completely selective formation of azafulleroid **3b** was achieved when 1.6 equivalents of **1b** were used (Table 1, entry 8).

To investigate the reaction pathway, isolated *N*-tosylaziridinofullerene **2a** and MS4A were heated in toluene under reflux, but the reaction did not proceed at all. In contrast, when **2a** was treated with *N*-tosylated chloramine **1a** under reflux in the presence of MS4A, *N*-tosylazafulleroid **3a** was produced (Table 2, entry 1), indicating that **3a** is formed from **2a**.

Treatment of **2a** with chloramine **1b**, which has a benzenesulfonyl group, under the same conditions gave a mixture of **3a** and *N*-benzenesulfonylaziridinofullerene **2b**. Extending the reaction time not only increased the yield of **3a** and consumption of **2b**, but also produced *N*-benzensulfonylazafulleroid **3b**. Interestingly, a catalytic amount of chloramine was found to be effective for the rearrangement. For example, **2a** was treated with 10 mol% of **1b** in the presence of MS4A in toluene at reflux for 5 h to give **3a** in 73% yield (Table 2, entry 4).

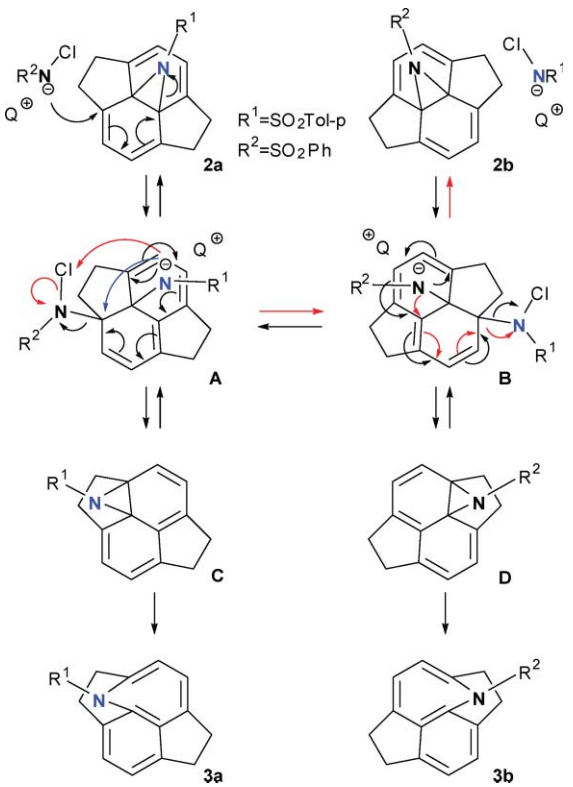
Based on these results, a mechanism for the rearrangement of aziridinofullerene is proposed as follows (Scheme 2, illustrated by a part of fullerene).

Table 2 Rearrangement of aziridinofullerene with chloramines



Entry	Chloramine (equivalents)	Time/min	Yield (%)[a] **3a**	**3b**	**2a**	**2b**
1	**1a** (1.0)	10	37[b]	—	20[b]	—
2	**1b** (1.0)	10	5	0	60	9
3	**1b** (1.0)	30	62	15	9	0
4	**1b** (0.1)	300	73	0	11	0

[a] Determined by ^{1}H NMR. [b] Isolated yields.



Scheme 2 Plausible pathway for the rearrangement.

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First, the most strained carbon[12] on aziridinofullerene **2a** is attacked by a chloramine to give diaminated intermediate **A**. The reaction, illustrated by the curved black arrows in intermediate **A** (π-conjugated S_N2' type reaction), leads to thermodynamically stable azafulleroid **3a** through closed, [5,6]-bridged intermediate **C**. An alternative route to **C**—an S_N1-type reaction (shown by the curved blue arrow), elimination of Cl and the R^2-substituted nitrogen prior to attack of the nitrogen anion—should be considered. The alternative path, shown by the curved red arrows in **A**, generates intermediate **B** *via* chlorine atom transfer. Intermediate **B** reacts in the same way as **A** to afford **2b** and **3b**. Although the function of MS4A is unclear at present, the ability to eliminate nitrogen anions generated *in situ* may be enhanced by the sodium cation in MS4A.

In summary, the present study has established a new chloramine-based aziridination of C_{60} and demonstrated an unprecedented rearrangement of aziridinofullerene to azafulleroid using a combination of chloramine and MS4A. The method has sufficient possibility for the synthesis of diverse aziridinofullerenes and azafulleroids using *N*-chloro-*N*-sodio derivatives.[13] Although the function of MS4A requires clarification, this is the first example of the ionic introduction of an N_1 unit to C_{60} and the reagent-assisted rearrangement of the product. Work along this line, as well as the expansion of the generality of the reaction, is currently under way.

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