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Exploring the photoinduced electron transfer reactivity of aza[60]fullerene iminium cation

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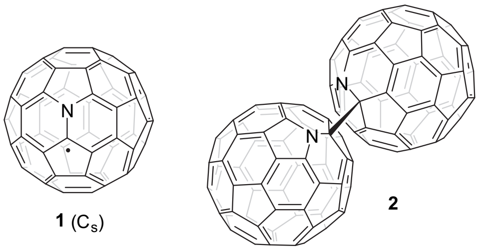
ABSTRACT

Photolysis of $(C_{59}N)_2$ solutions in the presence of neutral π-donors, such as arenes and electron-rich alkenes leads to a series of novel aza[60]fullerene monoadducts. The key step of the reaction involves a photoinduced electron transfer from the donor molecule to the iminium cation of aza[60]fullerene, followed by radical coupling of the resulting aza[60]fullerenyl radical with an intermediate stabilized radical derived from the substrate. This type of reactivity has been proven efficient with arenes having oxidation potential higher than about 1.5 V. Simple olefins, such as tri- and tetra-methylethylene, as well as cyclohexene, can also participate in this kind of photoinduced electron transfer-initiated reaction with $C_{59}N^+$, affording the corresponding aza[60]fullerene derivatives. In the case of 2-methoxyprop-1-ene, 2,4-hexadiene, and β,β-dimethylstyrene, [2+2] cycloaddition reactions with the aza[60]fullerene carbon shell dominate, leading to a mixture of unidentified multiadducts.

1. Introduction

Despite the very rich chemistry of C_{60} and the great number of functionalization techniques that have been developed over the years,[1] similar progress regarding its nitrogen substituted counterpart, aza[60]fullerene (**1**, Fig. 1), has been hampered thus far by the low symmetry of the heterofullerene sphere and by the fact that aza[60]fullerene is isolated as a dimer (**2**, Fig. 1).[2] In other words, the typical fullerene reactions can take place on any of the [6,6] double bonds of the two balls, affording complicated mixtures of isomers that are impossible to isolate and characterize. For example, one single addition on a [6,6] double bond in **2** can lead to 16 distinct isomers. As a result, only a few methods for the synthesis of well-defined aza[60]fullerene adducts are known at present.[3]



1 (C_s)

2

Fig. 1. Azafullerenyl radical $C_{59}N^•$ (**1**) and azafullerene dimer $(C_{59}N)_2$ (**2**).

The trapping of the azafullerenyl radical **1** was initially utilized to afford adducts **3** and **4** (Fig. 2); radical **1** was produced from dimer **2** either thermally or photochemically in the presence of a hydrogen atom donor, such as tributyl-tinhydride[4] or diphenylmethane,[5] respectively. In the same way, 9-alkyl-substituted fluorenes, 9,10-dihydroanthracene, and xanthene gave the corresponding monoadducts **5**, **6**, and **7** (Fig. 2).[6] A free radical chain mechanism has been proposed for the production of these aza[60]fullerene derivatives.[5–7]

However, the most efficient way to prepare aza[60]fullerene monoadducts involves the thermal treatment of the dimeric $(C_{59}N)_2$ in the presence of air and excess toluene-*p*-sulfonic acid (*p*-TsOH), a procedure that oxidizes the produced azafullerenyl radical **1** to aza[60]fullerene iminium cation $C_{59}N^+$ (**8**, Scheme 1), which is isoelectronic to C_{60}. This entity can be easily trapped by nucleophiles, such as electron-rich aromatics,[8,9] enolizable carbonyl compounds,[10] as well as alcohols and olefins,[11] furnishing the corresponding azafullerene derivatives (Scheme 1). The presence of both the oxygen and the acid is crucial for the above reactions to take place. It has been proposed that oxygen acts as the oxidizing agent, whereas toluene-*p*-sulfonic acid probably traps the reduced oxygen species and adjusts the solution's pH.[8]

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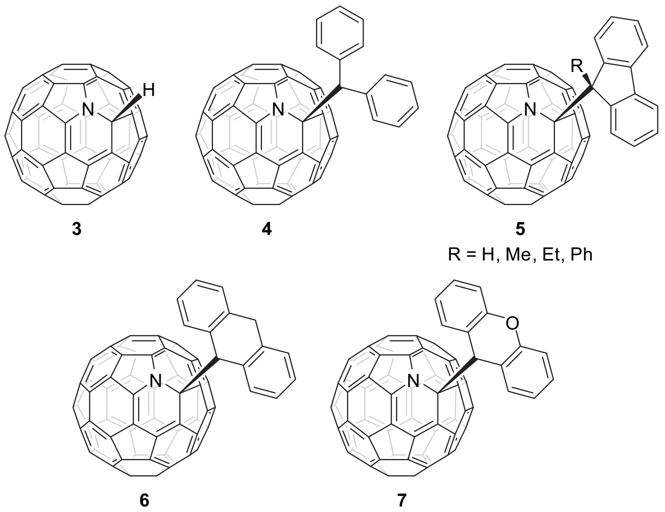
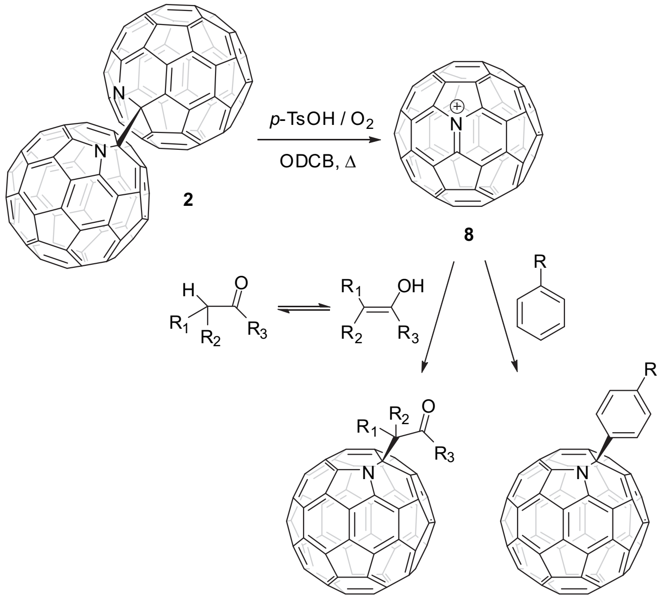


Fig. 2. Hydroaza[60]fullerene $C_{59}HN$ (**3**) and aza[60]fullerene monoadducts $C_{59}(CHPh_2)N$ (**4**), **5**, **6**, and **7**.



Scheme 1. Aza[60]fullerene iminium cation reactivity.

It is also worth mentioning that aza[60]fullerene multiadducts[12] have been successfully prepared and characterized starting from open-cage fullerene derivatives.[13]

Arene donors[14] as well as electron-rich olefins[15] are well-known for their ability to photochemically add to iminium cations of the general type **9** (Fig. 3). The mechanism that has been established for these reactions involves a photoinduced electron transfer (PET) from the π-system of the arene/olefin to the single excited state of the iminium cation in the first step, followed by the coupling of the two resulting radicals. The structural similarity between conventional iminium cations and aza[60]fullerene iminium cation **8** (Fig. 3) prompted us to investigate the $(C_{59}N)_2$ reactivity toward π-electron donors under photochemical conditions. Herein, we present the photochemical addition of benzyltrimethylsilanes and electron-rich alkenes to $C_{59}N^+$ through a PET-initiated chain mechanism.

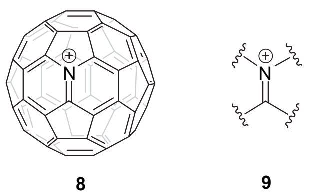
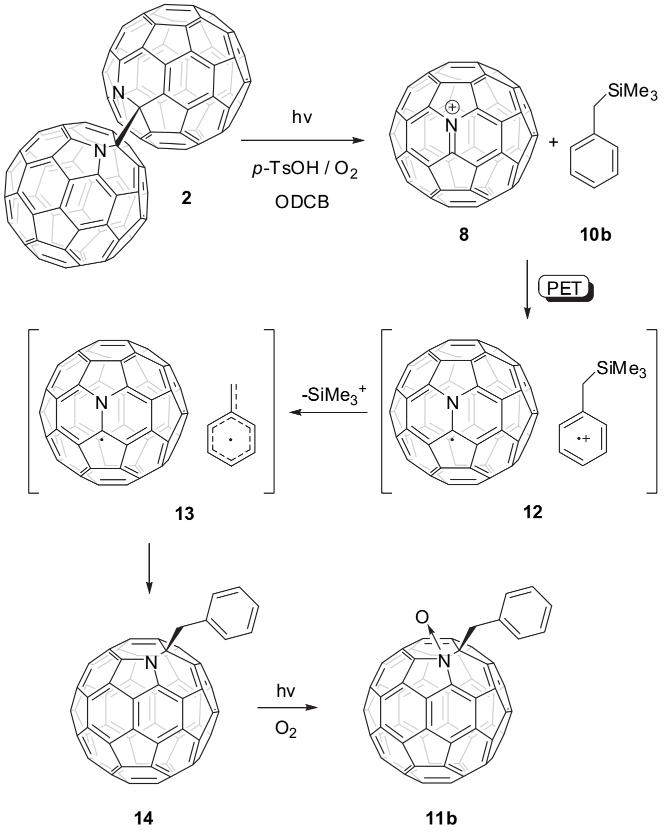


Fig. 3. Structural resemblance of aza[60]fullerene carbocation **8** with iminium cations in general (**9**).

2. Results and discussion

2.1. Photoinduced electron transfer reactions between iminium cation $C_{59}N^+$ and substituted benzyltrimethylsilanes

In a preliminary communication, we have reported that photochemically generated aza[60]fullerene iminium cation **8** reacts with benzyltrimethylsilane (**10b**) to give monoadduct **11b** (Scheme 2).[16] $(C_{59}N)_2$, together with a large excess of benzyltrimethylsilane, was irradiated in an *o*-dichlorobenzene (ODCB) solution in the presence of air and *p*-TsOH. After semi-preparative HPLC purification of the crude product, adduct **11b** was isolated in 28% yield. The proposed mechanism for the formation of **11b** is illustrated in Scheme 2. Iminium cation **8** derives from the oxidation of azafullerenyl radical **1**, which is generated by the photochemical homolysis of $(C_{59}N)_2$. Next, the key step of this reaction sequence, involving a photoinduced electron transfer from benzyltrimethylsilane **10b** to iminium cation **8**, affords radical cation pair **12**. Subsequent loss of the SiMe$_3^+$ group leads to the neutral radical pair **13**.[14,15] Adduct **11b** is eventually formed after radical coupling in **13** and self-sensitized photooxygenation[17] of the resulting intermediate **14**.



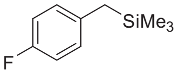
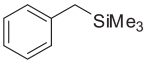
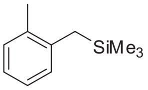
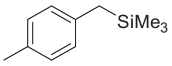
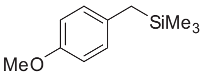
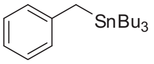
Scheme 2. The photoinduced electron transfer reaction between $C_{59}N^+$ (**8**) and benzyltrimethylsilane (**10b**) affording **11b**.

In the same context, Yoshida and co-workers have more recently reported the reaction of an electrochemically generated *N*-acyliminium ion pool with a series of benzylsilanes.[18] In agreement with the discussion above, they proposed that the reaction proceeds through a chain mechanism initiated by a single electron transfer

(SET) from benzylsilane to *N*-acyliminium cation, followed by desilylation of the formed benzylsilane radical cation.

With the aim of further studying the PET reactivity of iminium cation **8** toward benzyltrimethylsilanes of various oxidation potentials, we synthesized the series of benzyltrimethylsilanes depicted in Table 1 (**10a**,**c**–**e**), which are substituted with electron-withdrawing or electron-donating moieties. In Table 1 we also provide the oxidation potentials for these benzylsilanes. The lower the oxidation potential of a substrate, the higher its reactivity with formal iminium cations.[18] Benzyltributylstannane (**15**, Table 1) was also included in our studies. Due to its lower oxidation potential, in comparison with benzylsilanes **10a**–**e**, this compound was expected to be the most reactive toward aza[60]fullerene iminium cation **8**.

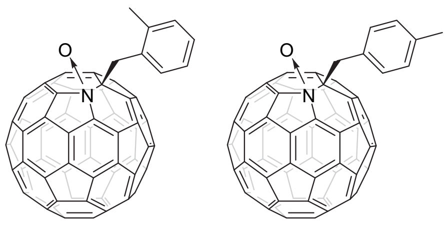
Table 1
Oxidation potentials of benzyltrimethylsilanes **10** and benzyltributylstannane **15**

Substrate	Oxidation potential (V)[a]
 **10a**	1.68
 **10b**	1.68
 **10c**	1.62
 **10d**	1.55
 **10e**	1.37
 **15**	1.24

[a] Taken from Ref. 18.

All reactions were performed according to the experimental conditions utilized in the preparation of adduct **11b**.[16] We initially chose to study the photoinduced reaction of (4-fluorobenzyl)trimethylsilane (**10a**) with **8**. As shown by HPLC analysis, azafullerene dimer is slowly consumed during this reaction, though without affording the corresponding monoadduct, at least in a detectable amount. Given that **10a** has the same oxidation potential as **10b** (vide supra), this is a rather surprising observation. The lack of aza[60]fullerene monoadduct formation in this case can only be attributed to the existence of the fluorine substituent, i.e., the electronics of **10a**, which, nevertheless, are not translated into a higher oxidation potential.

Next, we examined the reactivity of trimethyl(2-methylbenzyl)silane (**10c**) and trimethyl(4-methylbenzyl)silane (**10d**). Adducts **11c** and **11d** (Fig. 4) were isolated, respectively, in about 10% yield. Unlike most known fullerene derivatives, the solubility of these adducts in CS_2 was rather poor. A representative ^1H NMR spectrum of derivative **11d** is presented in Fig. 5.



11c **11d**

Fig. 4. Aza[60]fullerene monoadducts **11c** and **11d**.

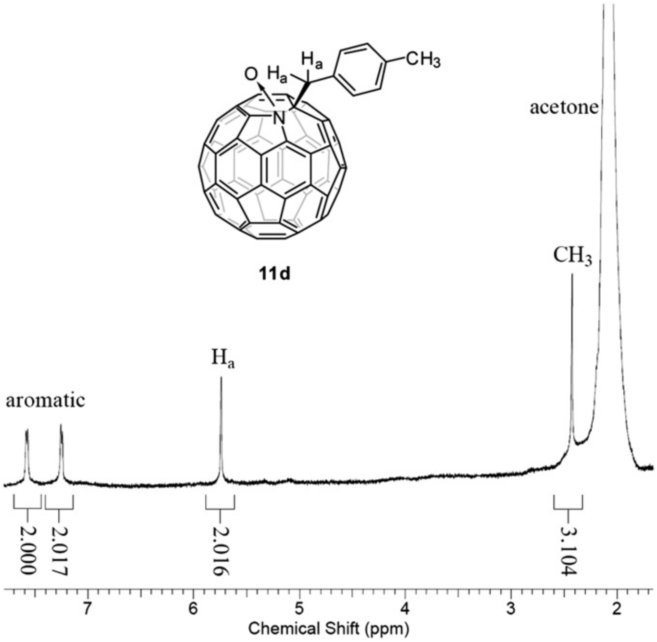


Fig. 5. ^1H NMR (500 MHz, acetone-d_6/CS_2) spectrum of **11d**.

(4-Methoxybenzyl)trimethylsilane (**10e**) and benzyltributylstannane (**15**) were also subjected to PET reaction conditions in the presence of in situ generated aza[60]fullerene iminium cation. Taking into account the low oxidation potential of these compounds (Table 1), their reactions with $C_{59}N^+$ were anticipated to proceed smoothly furnishing the corresponding azafullerene monoadducts. Nevertheless, as was clearly shown by HPLC analysis, azafullerene dimer **2** was gradually consumed upon irradiation without leading to the desired products. In this respect, irradiation of C_{60} solutions in the presence of benzyltrialkylstannanes, such as **15**, is known to lead to single electron transfer from the stannanes to the fullerene skeleton, affording the radical anion of C_{60} ($C_{60}^{\bullet -}$).[19] We speculate that similar electron transfer reactions occur in the case of $C_{59}N^+$; however, these reactions are obviously not taking place selectively on the iminium cation segment of the cage, in order to afford the corresponding α-amino radical/radical cation pair (**12** in Scheme 2), but, instead, on the carbon shell of $C_{59}N^+$ leading to a complex mixture of multiadducts, difficult to identify and isolate. It therefore seems that the enhanced efficiency with which **10e** and **15** can lose one electron turns out to be a disadvantage in the case of their PET reactions with $(C_{59}N)_2$.

2.2. Photoinduced electron transfer reactions between iminium cation $C_{59}N^+$ and electron-rich olefins. Photochemical attachment of aliphatic chains on the azafullerene core

As already mentioned in the introduction, simple alkenes are known to photochemically react with iminium cations.[15] In an earlier work, Mariano and co-workers have reported that irradiation of methanolic solutions containing iminium cation salts together with unsaturated compounds such as isobutylene, cyclohexene, methyl β,β-dimethylacrylate, or 1,3-butadiene, leads to the corresponding addition products. The established reaction mechanism involves a photoinduced electron transfer from the π-system of the alkene to the single excited state of the iminium cation.[15a]

The applicability of this functionalization methodology in the field of azafullerene chemistry was studied by replacing formal iminium cations with aza[60]fullerene iminium cation **8** and applying PET reaction conditions in the presence of olefins **16**–**24** (Fig. 6). The experimental procedure that was followed was the same as in the case of benzylsilanes discussed earlier: $C_{59}N^+$ was photochemically produced in situ from $(C_{59}N)_2$, in an ODCB solution and in the presence of *p*-TsOH, oxygen, and the olefin.

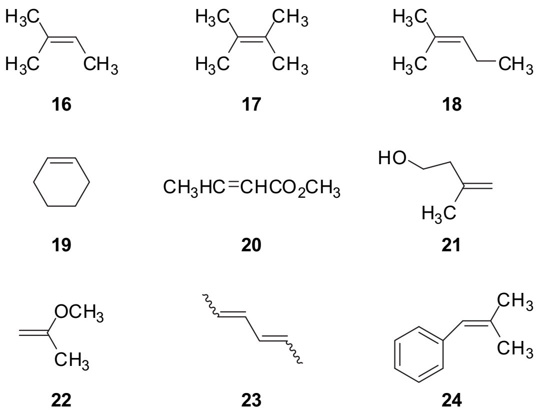
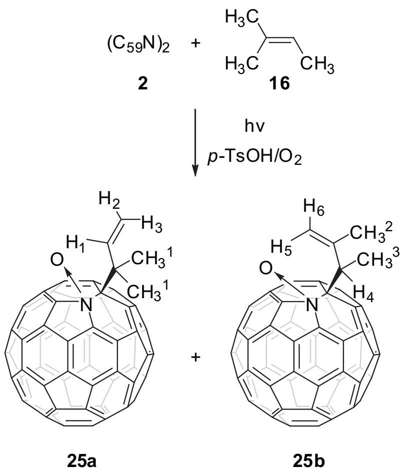


Fig. 6. Olefin substrates **16**–**24**.

The reaction of aza[60]fullerene dimer (**2**) with trimethylethylene (**16**) gave essentially one new peak in the corresponding HPLC chromatograms, attributed to a new aza[60]fullerene adduct. This adduct was isolated from the reaction mixture by column chromatography (SiO_2, toluene) and further purified by utilizing a semi-preparative HPLC column. The same isolation and purification procedure was followed for all azafullerene adducts we report in this section.

The new derivative was characterized by means of ^1H, ^1H–^1H COSY, and HMQC NMR experiments, and found to consist of the two inseparable isomers **25a** and **25b** (Scheme 3) in a ∼2.2/1 molar ratio. A representative ^1H NMR spectrum (500 MHz, $CDCl_3/CS_2$) of the **25a**/**25b** mixture is displayed in Fig. 7. The resonances between 5.1 and 6.6 ppm correspond to the vinylic protons of both isomers. Hence, the H_1 proton of **25a** resonates at 6.47 ppm as a doublet of doublets, because of its coupling with the two geminal protons H_2 (J_{cis}=10.5 Hz) and H_3 (J_{trans}=17.5 Hz); H_2 and H_3 protons are coupled with H_1 appearing as doublets at 5.40 (J_{cis}=10.5 Hz) and 5.58 ppm (J_{trans}=17.5 Hz), respectively. Furthermore, the singlet at 5.20 ppm corresponds to one of the two geminal protons of **25b** (H_5 or H_6), whereas the peak of the other germinal proton overlaps with H_2 at about 5.40 ppm. The allylic proton of **25b** (H_4) is observed as a quartet at 5.44 ppm (*J*=6.5 Hz), due to the splitting from the methyl group CH_3^3. Note that H_4 resonates at lower fields in comparison to typical allylic protons because besides being allylic, it is also next to the azafullerene sphere, and, therefore, suffers further deshielding. Both CH_3^1 methyl groups appear as a singlet at 1.86 ppm, the CH_3^2 group resonates also as a singlet at 2.12 ppm, while the CH_3^3 methyl group is split by H_4 into a doublet (*J*=6.5 Hz) observed at 1.72 ppm.



Scheme 3. Photochemical addition of olefin **16** to azafullerene dimer **2**.

According to what we have already discussed above, concerning the photoinduced electron transfer reactions of iminium cations, the formation of the two isomers (**25a** and **25b**, Scheme 3) can be explained on the basis of the mechanism depicted in Scheme 4: light-promoted electron transfer from the double bond of **16** to $C_{59}N^+$ leads to the formation of the radical cation pair **26**. Next, proton H_a or either proton H_b or H_c can be abstracted, affording the neutral radical pair **27a** or **27b**, respectively. Finally, coupling of the allylic radicals in **27a** and **27b** with azafullerenyl radical $C_{59}N$• and self-photooxygenation[17] of the resulting azacompounds affords final products **25a** and **25b**, respectively.

The mechanism proposed in Scheme 4 reveals an interesting feature of the addition reactions between olefins and aza[60]fullerene iminium cation (**8**). In particular, radical pairs **27a** and **27b** lead to the final products after the attachment of $C_{59}N$• to the most substituted end of the intermediate allylic radical. If radical coupling at the least substituted allylic carbon had taken place simultaneously, derivatives **25a′** and **25b′** (Fig. 8) would have been formed as well. However, these derivatives were not detected in the ^1H NMR spectra of the reaction products. On the basis of solely stereochemical hindrance criteria, this result is rather surprising and unanticipated. Indeed, it is well-established that similar radical couplings between α-amino radicals and allylic radicals, produced from allylsilanes $R_2C{=}CHCH_2SiR_3$, take place exclusively at the least substituted terminus.[20]

The exclusive formation of adducts **25a** and **25b**, instead of their isomers **25a′** and **25b′**, can be explained in terms of the greater stability of a tertiary or a secondary radical versus a primary one (Scheme 5). Also note that a wide variety of free radicals can multiply add to fullerene molecules leading to free radical mono- and multiadducts.[21] That being said, the primary radicals in radical pairs **27a** and **27b** (Scheme 5) are very unstable and, therefore, highly reactive toward the aza[60]fullerene carbon cage. Consequently, no regioselectivity is expected during their addition reactions, and multiple addition products rather than monoadducts **25a′** and **25b′** will be formed. The stabilized secondary and tertiary radicals (Scheme 5) on the other hand, are less reactive and can add regioselectively to the α-amino radical center of azafullerenyl radical **1**, affording compounds **25a** and **25b** that are eventually isolated. In any case, and beyond the above rationalization, the influence of stereoelectronic effects on the observed regioselectivity cannot be ruled out.

Moreover, the formation of isomer **25a** at a greater percentage than **25b** (**25a**/**25b**=∼2.2/1) is observed due to the enhanced stability of the tertiary radical (in comparison with the secondary one). This means that either the formation of radical pair **27a**, bearing the tertiary radical, is favored over the formation of **27b** (i.e., H_a^+ abstraction is more favorable than H_b^+ or H_c^+ abstraction), or that the tertiary radical adds to the α-amino radical center of **1** with an enhanced regioselectivity in comparison with the secondary one. Of course, both scenarios may occur simultaneously.

The photochemical reactions of aza[60]fullerene iminium cation (**8**) with substrates **17** and **18** (Fig. 6) have also furnished the corresponding new adducts **28**, **29a**, and **29b** illustrated in Fig. 9. We

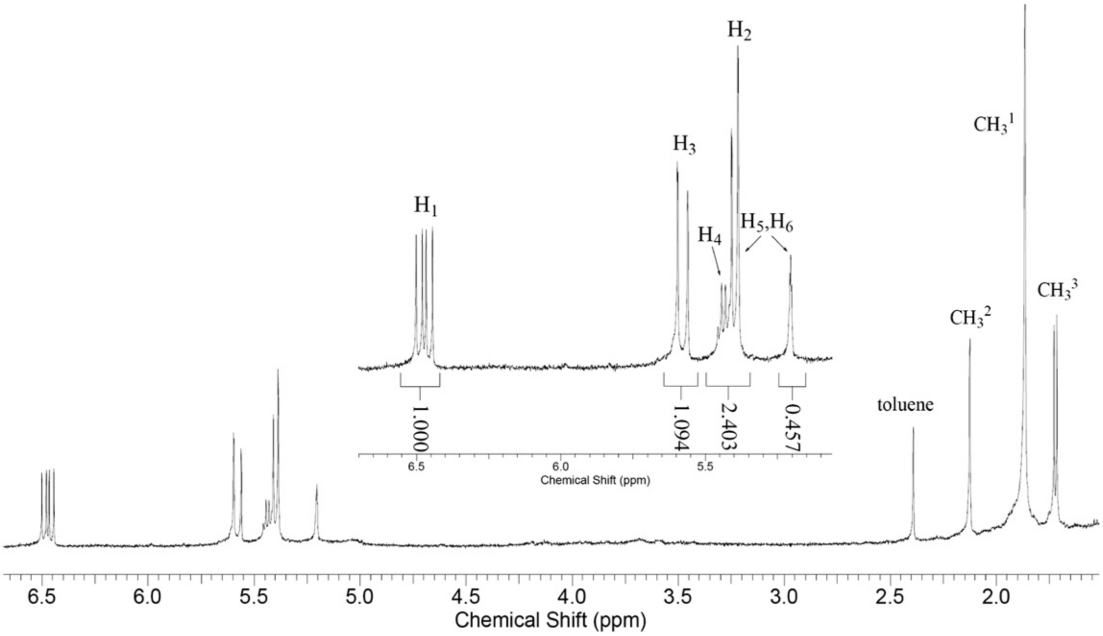
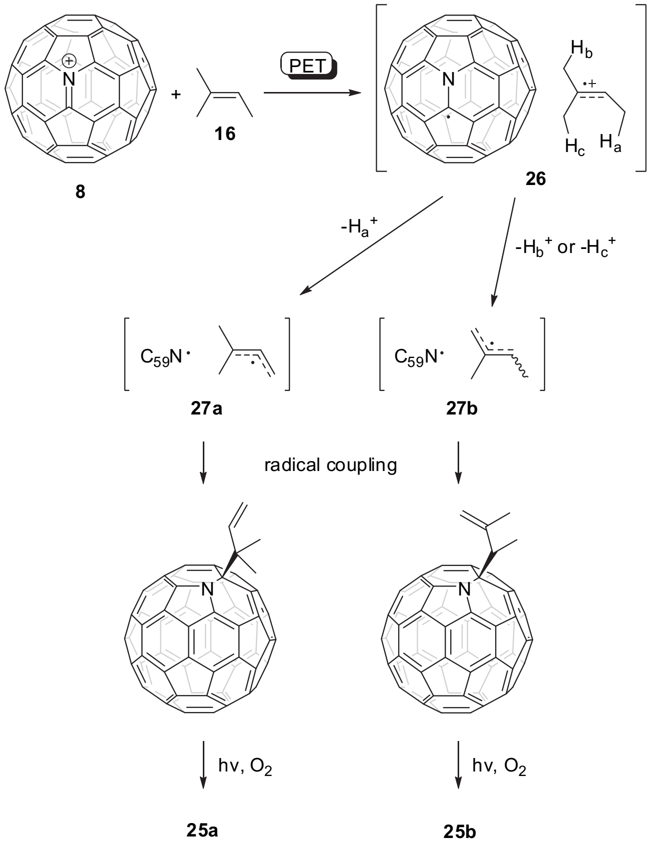
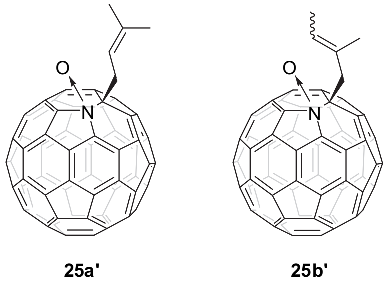


Fig. 7. ^{1}H NMR spectrum (500 MHz, $CDCl_3/CS_2$) of **25a**/**25b** mixture.

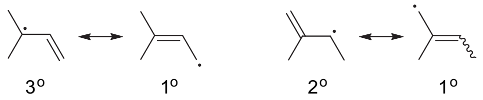


Scheme 4. Proposed mechanism for the photochemical addition of **16** to iminium cation $C_{59}N^+$.



25a′ **25b′**

Fig. 8. Hypothetical monoadducts **25a′** and **25b′** (not observed).

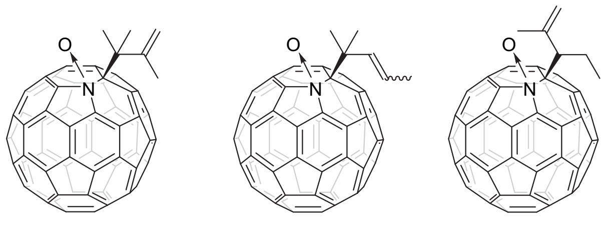


Scheme 5. Resonance structures of the allylic radicals in radical pairs **27a** and **27b**.

speculate that these products are also formed via the mechanistic pathway shown in Scheme 4. Tetramethylethylene (**17**), due to its high symmetry, led to a single product (**28**), whereas **18**, similarly to **16**, gave a mixture of two isomers (**29a** and **29b**).

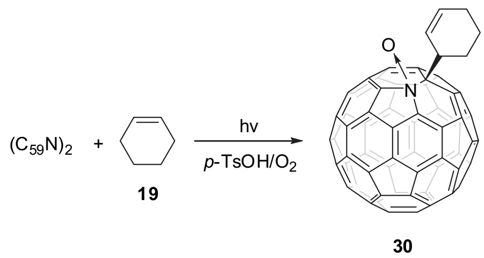
The photochemical addition of cyclohexene (**19**, Fig. 6) to $C_{59}N^+$ afforded aza[60]fullerene derivative **30** (Scheme 6), as identified by ^{1}H, ^{1}H–^{1}H COSY, and HMQC NMR experiments. Note that the thermal addition of the structurally similar cyclooctene to $C_{59}N^+$ has been reported earlier (Scheme 7).[11] This reaction has been proposed to proceed via the nucleophilic addition of cyclooctene to $C_{59}N^+$ (**8**), followed by proton elimination, and gives four isomeric $C_{59}N$/cyclooctene adducts (Scheme 7). These isomers supposedly derive after acid-catalyzed isomerization of the double bond on the cyclooctenyl ring of the aza-adduct. Under the PET conditions of our experiment, the formation of only one isomer has been achieved from the reaction of cyclohexene with $C_{59}N^+$; double bond isomerization of the cyclohexenyl ring in **30** does not take place in this case.

PET functionalization of $C_{59}N^+$ with compounds **20** and **21** (Fig. 6) was also attempted but proved to be unsuccessful. Instead, these reactions provided compounds **31** and **32**, respectively (Fig. 10). Apparently, acidic hydrolysis of the ester group in **20** produces a methanol molecule that attacks the azafullerene iminium cation to give adduct **31**. Product **32** is also the result of a nucleophilic attack of the hydroxyl group of **21** to cation **8**. Thus, nucleophilic attack to iminium cation **8** is a much more efficient process than photoinduced electron transfer, at least concerning the double bonds of alkenes **20** and **21**.

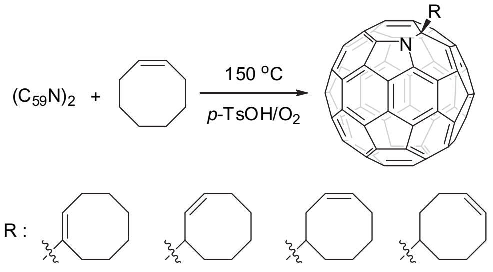


28 29a 29b

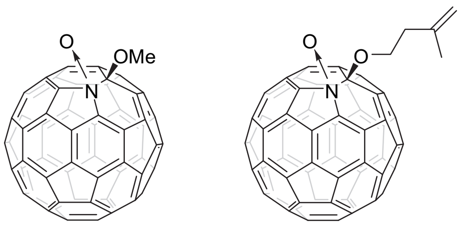
Fig. 9. Novel aza[60]fullerene derivatives **28**, **29a**, and **29b**.



Scheme 6. Photochemical addition of cyclohexene to $C_{59}N^+$.



Scheme 7. $C_{59}N$/cyclooctene isomers.



31 32

Fig. 10. Molecular structures for compounds **31** and **32**.

Finally, we also tested whether **22**–**24** (Fig. 6) exhibit PET reactivity against $C_{59}N^+$. The double bonds of these olefins are fairly electron-rich; however, their irradiation in the presence of $(C_{59}N)_2$ resulted in the formation of many different, unidentified multiadducts emanating from [2+2] cycloadditions on the aza[60]fullerene carbon core. This kind of reactivity is well-established for these substrates in their reactions with fullerene C_{60}.[22,23]

3. Conclusion

The results presented herein comprise the first detailed study on the photoinduced electron transfer reactivity of azafullerene iminium cation $C_{59}N^+$, the least developed azafullerene functionalization methodology. A series of arenes and electron-rich olefins were utilized as substrates. Arenes with oxidation potentials higher than about 1.5 V (benzyltrimethylsilane, trimethyl(2-methylbenzyl)silane and trimethyl(4-methylbenzyl)silane) are generally suitable for this reaction type. With benzyltributylstannane and benzyltrimethylsilanes having oxidation potentials lower than about 1.5 V, photoinduced electron transfer toward $C_{59}N^+$ occurs readily, though not solely on the iminium cation moiety of $C_{59}N^+$, leading to the formation of multiaddition products that are difficult to isolate and identify. In the second part of our study it was shown that simple olefins, such as tri- and tetra-methylethylene, as well as cyclohexene, also participate in photoinduced electron transfer-initiated reactions with $C_{59}N^+$, giving new aza[60]fullerene derivatives that bear small aliphatic chains. These adducts are isolated in relatively low yields (about 10%, see Experimental section)[24] because the unstable free radical species that are formed during the reaction are expected to attack the azafullerene carbon shell non-regiospecifically. Finally, relatively electron-rich alkenes, such as 2-methoxyprop-1-ene, 2,4-hexadiene, and β,β-dimethylstyrene, react with azafullerene iminium cation $C_{59}N^+$, albeit in a [2+2] cycloaddition mode, providing unidentified azafullerene multiadducts.

4. Experimental

4.1. General remarks

All photochemical reactions were carried out using a 300 W Xenon lamp as the light source and a Pyrex filter (>290 nm wavelength). Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AMX-500 MHz spectrometer in the appropriate solvent. Chemical shifts are reported in parts per million downfield from Me_4Si (δ=0 ppm), by using the residual solvent peak as an internal standard. Coupling constants (J) are in hertz. The purchased reagents and solvents were used as-received without further purification. High performance liquid chromatography (HPLC) analyses were carried out on a Cosmosil 5C18-MS-II (4.6 ID×250 mm) reverse phase column with detection at 326 nm. A mixture of toluene/acetonitrile (60/40) was used as eluent at 1 mL/min flow rate. Chromatography refers to flash column chromatography and was carried out on SiO_2 (silica gel 60, SDS, 230–400 mesh ASTM). Azafullerene adducts were further purified by HPLC using a semi-preparative Cosmosil 5PBB (10 ID×250 mm) normal phase column. A mixture of toluene/hexane (70/30) was used as eluent at 4 mL/min flow rate (detection at 326 nm).

Aza[60]fullerene $(C_{59}N)_2$,[6b] benzyltrimethylsilanes **10**,[18] and benzyltributylstannane **15**[18] were prepared according to published experimental procedures and were identified by comparing their spectra with those reported in the literature.[18,25,26]

4.2. General procedure for the photochemical reactions of aza[60]fullerene iminium cation $C_{59}N^+$

Aza[60]fullerene $(C_{59}N)_2$ **2** (20 mg, 13.8×10^{-3} mmol) together with a 35-fold excess of p-TsOH (90 mg, 0.48 mmol) were dissolved in 10 mL ODCB (HPLC grade). Next, 500 equiv of the π-donor (arene or olefin) was added and the solution was irradiated with the Xenon lamp while bubbling with a gentle stream of air. The temperature of the reaction was maintained at 0 °C using an ice bath. Reaction progress was followed by HPLC. All irradiations typically lasted from 2 to 3 h (dimer **2** was not completely consumed). After that, the reaction mixture was poured on a column of silica/toluene in order to neutralize p-TsOH and get rid of the azafullerene multiadducts that are insoluble in ODCB. Elution with toluene gave a brown-colored fraction containing the aza[60]fullerene adduct. The solvent was then removed in vacuo at 60 °C, and the remaining solid was washed and centrifuged four times with acetonitrile HPLC grade. Further purification of the reaction products was achieved by semi-preparative HPLC. All aza[60]fullerene derivatives were collected in about 10% isolated yield.

*4.2.1. Aza[60]fullerene adduct **11c**.* This adduct was isolated in about 10% yield (2.4 mg). Compound **11c**: mp>360 °C; ^{1}H NMR (500 MHz, acetone-d_6/CS$_2$): δ 7.3–7.0 (m, 4H), 5.81 (s, 2H), 2.69 (s, 3H) ppm.

*4.2.2. Aza[60]fullerene adduct **11d**.* This adduct was isolated in about 10% yield (2.2 mg). Compound **11d**: mp>360 °C; ^{1}H NMR (500 MHz, acetone-d_6/CS$_2$): δ 7.58 (d, J=7 Hz, 2H), 7.25 (d, J=7 Hz, 2H), 5.74 (s, 2H), 2.42 (s, 3H) ppm.

*4.2.3. Aza[60]fullerene adducts **25a** and **25b**.* This product mixture was isolated in 15% yield (3.3 mg). Compounds **25a**, **25b**: mp>360 °C; ^{1}H NMR (500 MHz, CDCl$_3$/CS$_2$): δ 6.47 (dd, J_{cis}=10.5 Hz, J_{trans}=17.5 Hz, 1H of **25a**), 5.58 (d, J_{trans}=17.5 Hz, 1H of **25a**), 5.44 (q, J=6.5 Hz, 1H of **25b**), 5.40 (d, J_{cis}=10.5 Hz, 1H of **25a**), 5.40 (s, 1H of **25b**), 5.20 (s, 1H of **25b**), 2.12 (s, 3H of **25b**), 1.86 (s, 6H of **25a**), 1.72 (d, J=6.5 Hz, 3H of **25b**) ppm.

*4.2.4. Aza[60]fullerene adduct **28**.* This adduct was isolated in 11% yield (2.5 mg). Compound **28**: mp>360 °C; ^{1}H NMR (500 MHz, CDCl$_3$/CS$_2$): δ 5.36 (s, 1H), 5.18 (s, 1H), 2.21 (s, 3H), 1.90 (s, 6H) ppm.

*4.2.5. Aza[60]fullerene adducts **29a** and **29b**.* This product mixture was isolated in 10% yield (2.2 mg). Compounds **29a**, **29b**: mp>360 °C; ^{1}H NMR (500 MHz, CDCl$_3$/CS$_2$): δ 6.05 (m, 1H of **29a**), 5.37 (s, 1H of **29b**), 5.37 (m, 1H of **29a**), 5.26 (s, 1H of **29b**), 5.21 (t, J=7 Hz, 1H of **29b**), 2.10 (s, 3H of **29b**), 1.91 (m, 2H of **29b**), 1.89 (d, J=5 Hz, 3H of **29a**), 1.84 (s, 6H of **29a**), 1.21 (t, J=7.5 Hz, 3H of **29b**) ppm.

*4.2.6. Aza[60]fullerene adduct **30**.* Derivative **30** was proven very labile as it decomposes when passed through the semi-preparative HPLC column. However, its crude ^{1}H NMR spectra, following silica gel chromatography, were quite clean and fortunately allowed its structure identification. Compound **30**: ^{1}H NMR (500 MHz, CDCl$_3$/CS$_2$): δ 6.24 (m, 1H), 6.17 (m, 1H), 5.43 (m, 1H), 2.62 (m, 1H), 2.37–2.00 (m, 4H), 1.88 (m, 1H) ppm.

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