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$C_{59}N^+$: A key intermediate in azaheterofullerene chemistry

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Abstract—The thermal treatment of the azaheterofullerene dimer $(C_{59}N)_2$ in the presence of oxygen and a nucleophilic trapping reagent leads to the facile and selective formation of a variety of monomeric adducts $C_{59}NR$ involving electronic rich aromatics, carbonyl compounds, alcohols and olefins as terminating addend. These investigations within the field of synthetic heterofullerene chemistry imply the presence of $C_{59}N^+$ as an important key intermediate.

1. Introduction

In 1995, the preparative chemistry of heterofullerenes began with the first synthesis and isolation of the nitrogen heterofullerene dimer $(C_{59}N)_2$ (**1**), elaborated independently by Wudl et al. and our group using two different strategies starting with parent C_{60}.[1,2] The availability of $(C_{59}N)_2$ (**1**) in bulk quantities allowed further chemical transformations and the detailed investigation of physical properties.

The substitution of one carbon atom of the fullerene framework with nitrogen leads to the formation of an open-shell system. Consequently, the simplest nitrogen heterofullerene can only be isolated as the dimer **1**. In this compound two $C_{59}N$ moieties are connected by an sp^3-carbon adjacent to the nitrogen atom.[3]

Of preparative interest are monomeric substitution products where one $C_{59}N$ moiety is replaced by a substituent. Such monomers containing suitable side chains can exhibit higher solubilities than the parent dimer **1**. This is favorable for the investigation of subsequent derivatizations and the design of materials involving heterofullerene building blocks. So far two important routes for the synthesis of monomeric $C_{59}N$ derivatives have been developed (Scheme 1).

Wudl et al. showed that a homolytic cleavage of the interdimer C–C bond, which can be achieved thermally or photochemically, leads to the monomeric radical $C_{59}N$ (**2**).[4] This species can either dimerize back to **1** or can be trapped with suitable radical sources to form monomeric $C_{59}N$ derivatives. For instance, $C_{59}NH$ (**3**), where one $C_{59}N$ moiety is substituted with an H-atom, was obtained by the thermal treatment of **1** in 1,2-dichlorobenzene (ODCB) in the presence of $^n Bu_3SnH$.[5] Other monomeric derivatives like **4** are also available by radical reactions of **2**.[4] We recently elaborated another reaction sequence to obtain monomeric $C_{59}N$ systems. Treatment of **1** with electron-rich aromatics, e.g. veratrole, in the presence of air and excess *p*-TsOH at 150°C causes the formation of arylated aza[60]fullerene derivatives like **5**.[6] In this reaction, the intermediate formation of $C_{59}N^+$ (**6**), which is isoelectronic to C_{60}, seems likely. $C_{59}N^+$ is presumed to be formed via thermal homolysis of the dimer, followed by oxidation of the radical (Scheme 2). Subsequently, the azafulleronium ion **6** undergoes an electrophilic aromatic substitution with the electron-rich aromatic compound. Due to steric restrictions only the formation of *para* substitution products (**8**) can be observed.

The oxidation is a critical step, since running the reaction in an argon atmosphere does not yield arylated products at all. The role of the *p*-TsOH is not yet clear. We assume that the redox potential of $C_{59}N/C_{59}N^+$ depends on the pH, since in the absence of the acid no reaction takes place.

In this contribution, we present full experimental details of a whole series of trapping experiments with different types of nucleophiles including further extension of reactions with enolizable carbonyl compounds reported in a preceding short communication.[7] These investigations strongly corroborate the presence of **6** as key intermediate and demonstrate the wide scope of these reactions with respect to heterofullerene functionalization. All monomeric $C_{59}N$ derivatives were isolated and fully characterized by MS, UV, IR and NMR spectroscopy. Moreover, we demonstrate that the oxidation of **2** leading to **6** can also be promoted by other oxidizing agents such as chloranil.

Keywords: fullerenes; azaheterofullerenes; Mannich reaction; enols.

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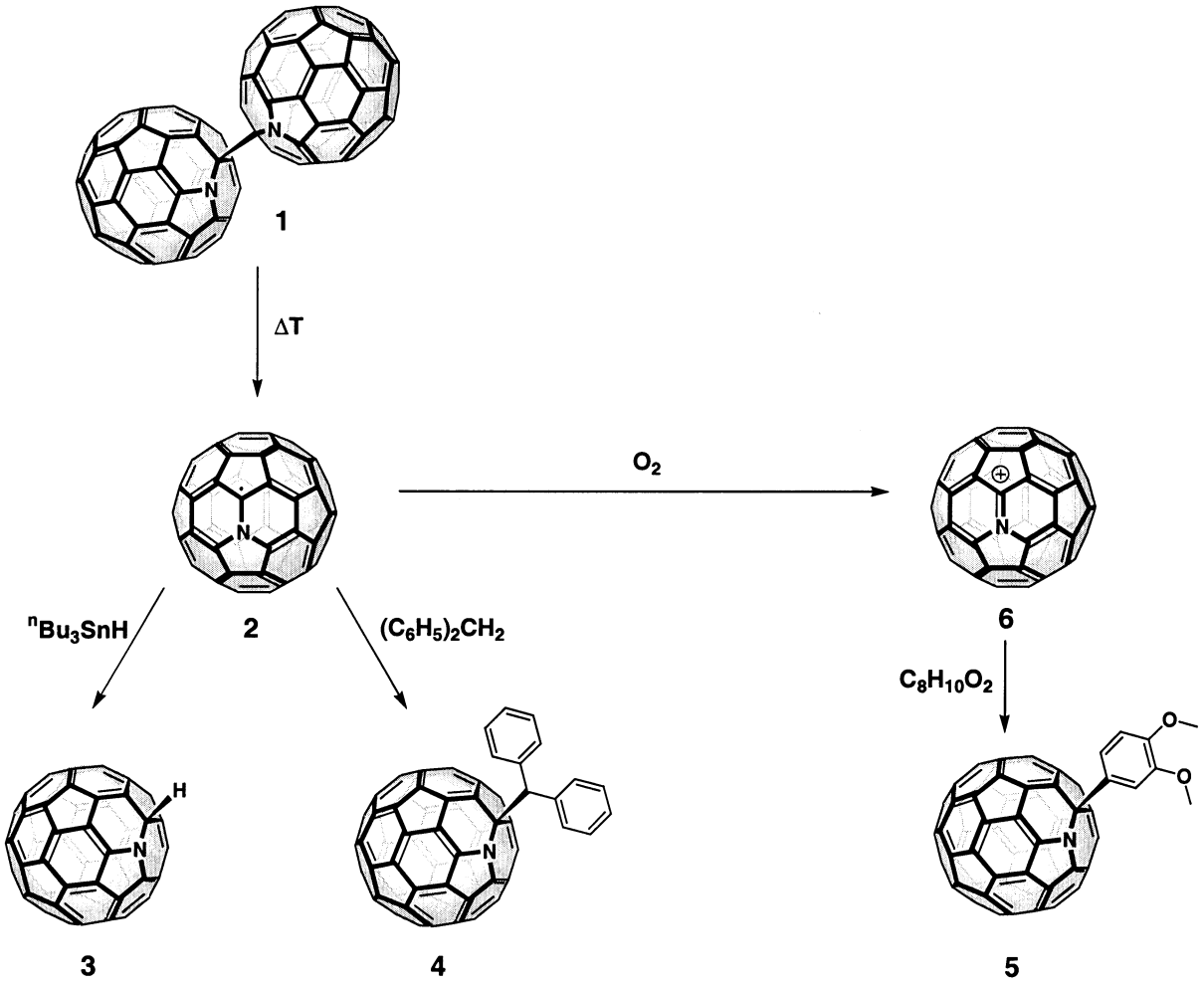
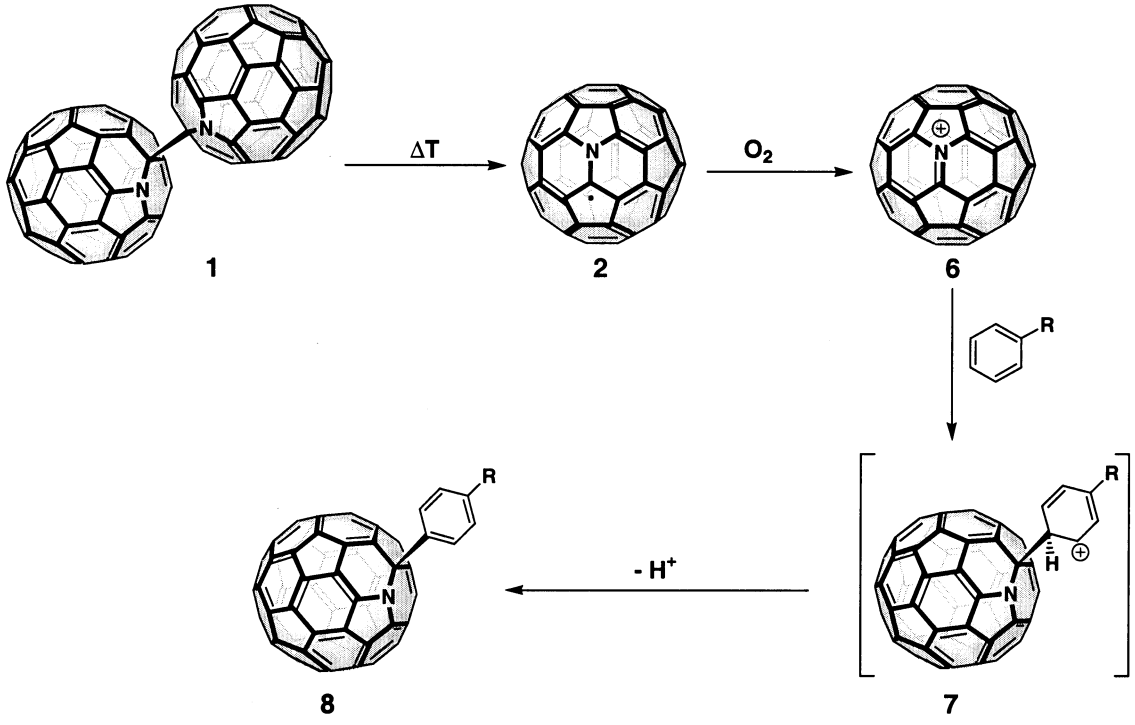
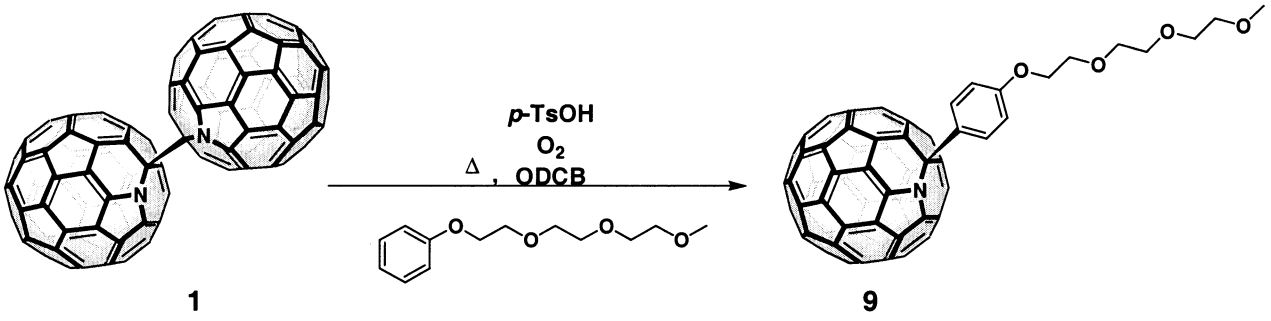


Scheme 1. Possible reaction pathways of **1** leading to monomeric structures.



Scheme 2. Formation of arylated heterofullerene derivatives.



Scheme 3. Synthesis of *p*-methoxy-ethoxy-ethoxy-ethoxy-hydroazafullerene **9**.

2. Results and discussion

2.1. Synthesis of a well soluble $C_{59}N$ derivative

The first monomeric $C_{59}N$ derivatives we prepared did not exhibit solubilities that were much higher than that of **1**. They hardly dissolve in most organic solvents. As a consequence, NMR-spectroscopic characterization and further chemical transformation of these compounds turned out to be difficult. This problem can be avoided by choosing a suitable side chain, for example as substituent of an aromatic trapping reagent. An aromatic system with a triethylenglycol substituent turned out to be a proper choice. The reaction of $(C_{59}N)_2$ with methoxy-ethoxy-ethoxy-ethoxy-benzene and *p*-TsOH in the presence of air at 150°C leads to the formation of *p*-methoxy-ethoxy-ethoxy-ethoxy-hydroazafullerene **9** in 82% yield (Scheme 3). The product fraction (R_f=0.46, silica gel, toluene/ethyl acetate 7:3) was isolated by flash chromatography on silica gel as olive-green colored band using toluene as eluent.

As mentioned above, the only reaction product is the *para* isomer. Compound **9** shows excellent solubility in organic solvents like toluene, dichloromethane, ODCB or carbon disulfide (more than 25 mg/ml) and therefore represents a suitable educt for further transformations of the $C_{59}N$ system.

2.2. Mannich functionalization of $C_{59}N$[7]

Mannich bases **10** and **11** were obtained in almost quantitative yield by the treatment of $(C_{59}N)_2$ in ODCB with 20 equiv. of acetone or acetophenone and 40 equiv. of *p*-TsOH at 150°C in a constant stream of air (Scheme 4).

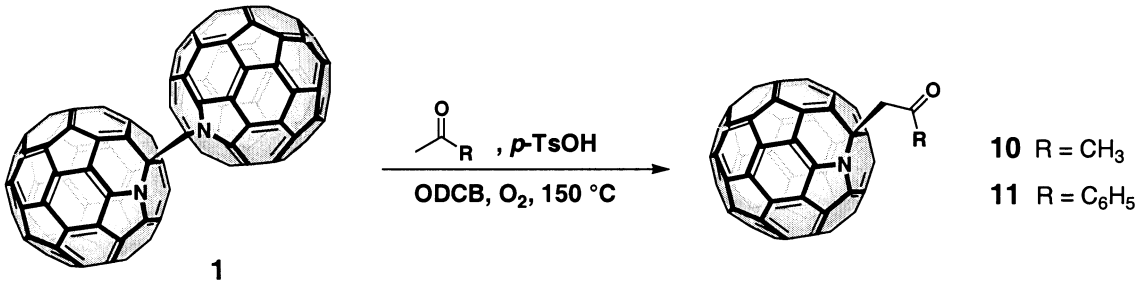
After 15 min, the conversion was completed. The isolation of the products was achieved by flash chromatography on silica gel using toluene as a mobile phase. Thereby **10** and **11** eluted as the least polar olive-green colored fractions. For the reaction of $(C_{59}N)_2$ with enolizable compounds we suggested the same mechanism (Scheme 5) as for the formation of arylated monoazaheterofullerene derivatives.[7]

In the presence of *p*-TsOH the ketones and aldehydes are in equilibrium with their enol forms. The intermediate cation $C_{59}N^+$ (**6**), formed by oxidation of the $C_{59}N$ radical (**2**), is able to attack the enol form of the ketone/aldehyde and after deprotonation the α-azafullerenated ketone/aldehyde (**13**) is formed.

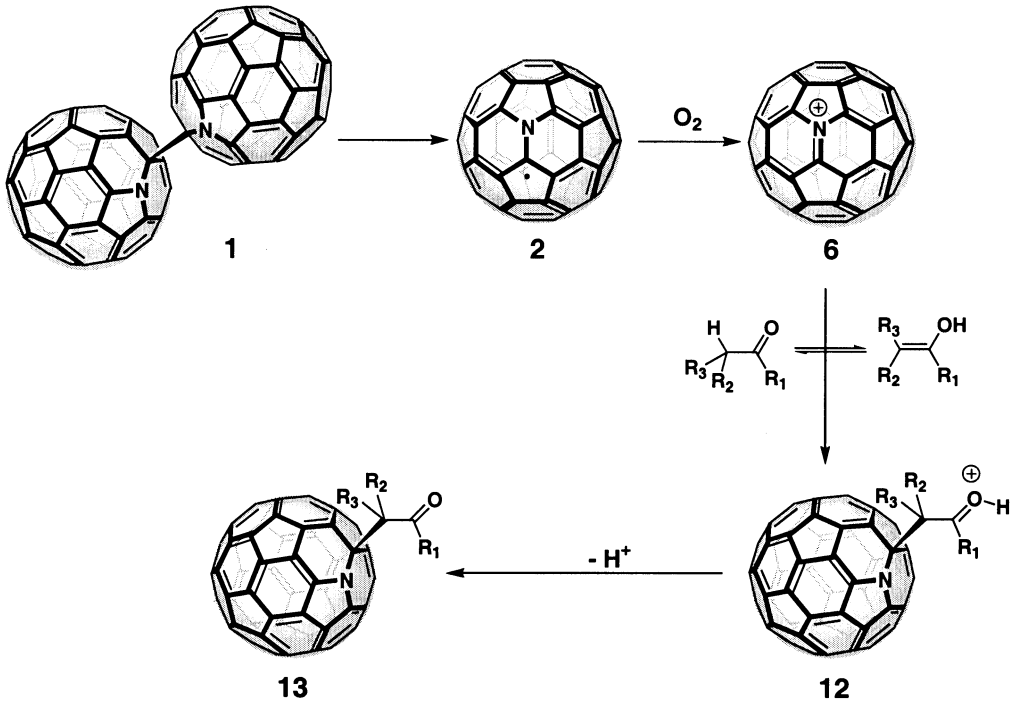
Acetophenone, a compound which offers an aromatic as well as an enolic moiety clearly shows preferred attack at the α-CH_3 position. This result is not surprising, since acetophenone is certainly not an electron rich aromatic system. This behavior can indeed be taken as another proof for our proposed reaction mechanism, i.e. the azafulleronium cation **6** being the reaction intermediate.

Treatment of **1** with aldehydes like propanal under the same experimental conditions also leads to the formation of the corresponding mannich bases like **14** (Scheme 6). Next to 1-azafullerenylpropanal (**14**) the aldol condensation product **15** was formed. The yield of **15** increases with longer reaction times at the expense of **14**. Consequently, the aldol condensation step takes place after compound **14** has been formed (Scheme 7). NOE NMR spectra showed that the isolated product **15** contains a double bond with the *E*-configuration exclusively.

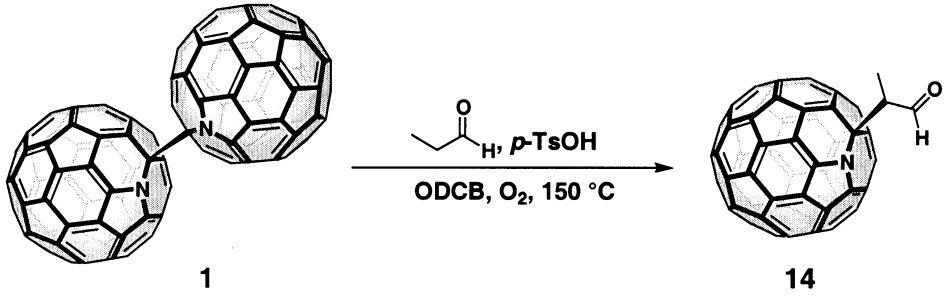
All $C_{59}N$ derivatives described above, which were obtained by the reaction of $(C_{59}N)_2$ with aldehydes or ketones, show



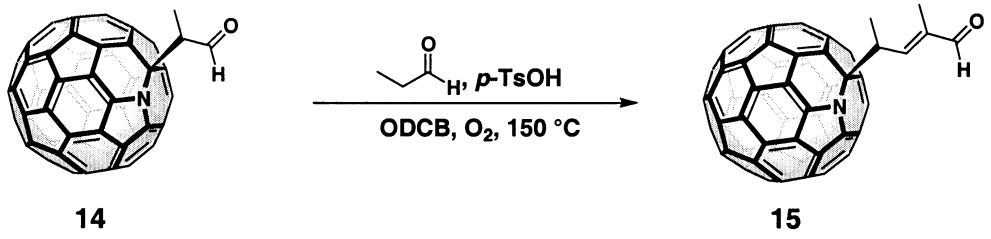
Scheme 4. Reaction of **1** with ketones; formation of α-azafullerenated ketones.



Scheme 5. Reaction mechanism of **1** with enolizable compounds.



Scheme 6. Formation of chiral 2-azafullerenylpropanal **14**.



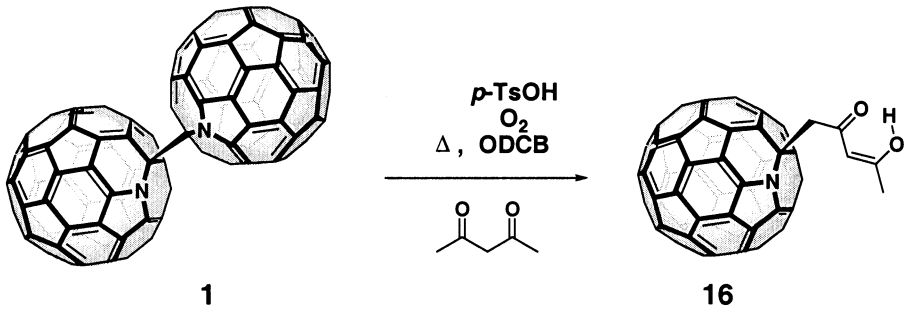
Scheme 7. Aldol condensation step leading to **15**.

comparatively high solubility in organic solvents and form olive green colored solutions.

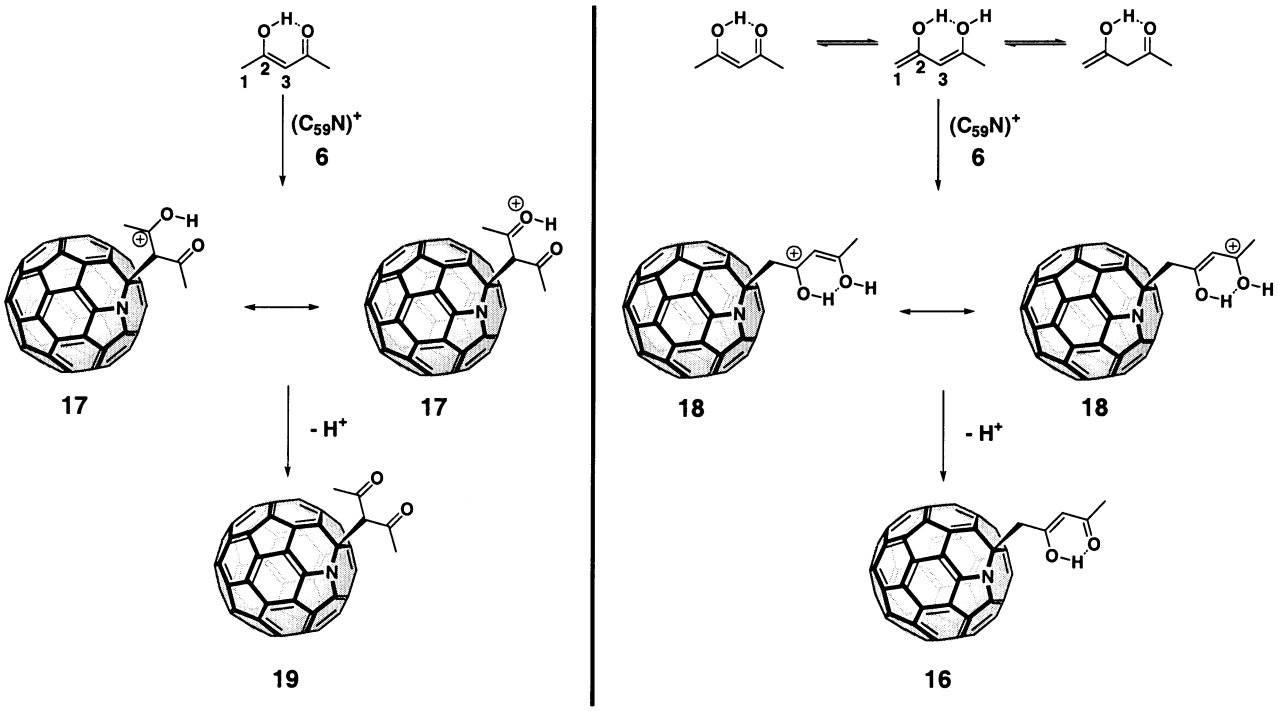
2.3. Reaction with 1,3-dicarbonyl compounds

Using acetylacetone as 1,3-dicarbonyl compound under reaction conditions described above leads to an unexpected product. Electrophilic attack of **6** at the central C-atom of acetylacetone containing the most acidic protons would lead to a symmetrical addition product. The ^{1}H NMR spectrum of the reaction product, however, is consistent with formation of **16**, since it shows, for example, the resonance of an olefinic proton at δ=6.2 ppm. Consequently, acetylacetone reacts with **1** leading to **16**, bearing the $C_{59}N$ moiety at a terminal carbon atom (Scheme 8).[7]

In principle, two reasons for the formation of the observed product **16** can be considered. First, sterical restrictions leading to a preferred attack of **6** to a terminal carbon atom of acetylacetone and second, the product formation could be controlled by thermodynamic stabilities of products and intermediates due to electronic factors. In order to achieve further insight into this question, we used heptane-3,5-dione, which is sterically more hindered at the



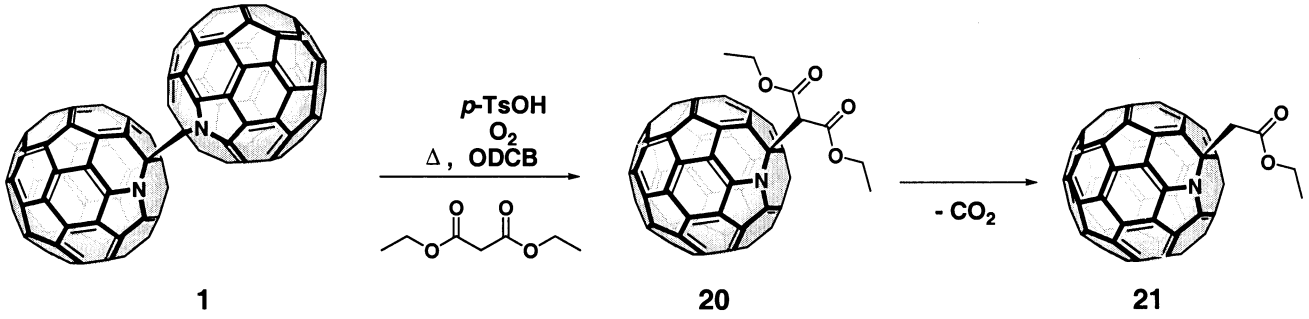
Scheme 8. Reaction with acetylacetone leading to **16**.



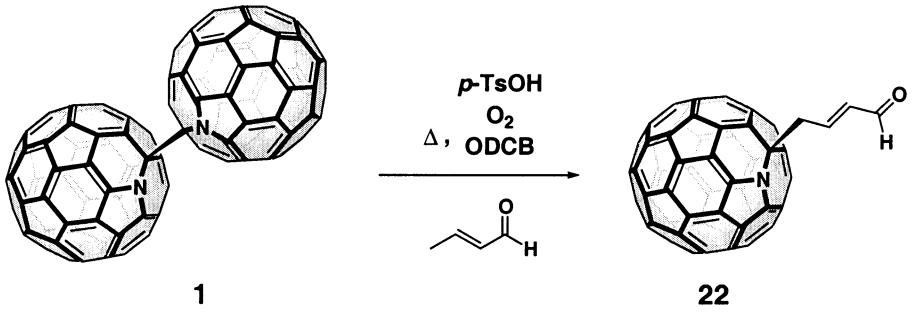
Scheme 9. Central versus terminal attack of **6** to a 1,3-dicarbonyl compound.

terminal carbon atom. We obtained a reaction mixture of three products, probably containing a bisadduct and two isomeric monoadducts. All three products show signals for olefinic protons at about $\delta=6.2$ in the ^{1}H NMR spectra, indicating that in all three cases $C_{59}N^+$ attacks the terminal carbon atom instead of the central one.[7] Consequently, we assume that electronic factors are responsible for the formation of the observed $C_{59}N$ derivatives. In Scheme 9 the central and the terminal attack of **6** to 1,3-dicarbonyl compounds are depicted.

Attack of **6** to C3 of acetylacetone leads to cation **17**, which is stabilized by an O-π-donor. For an attack at C1 one has to assume a tautomeric equilibrium of acetylacetone leading to an enolized C1 carbon atom. The attack at this C-atom leads to the intermediate **18**, which is a bis-donor substituted



Scheme 10. Products formed by the reaction of diethylmalonate with **1**.

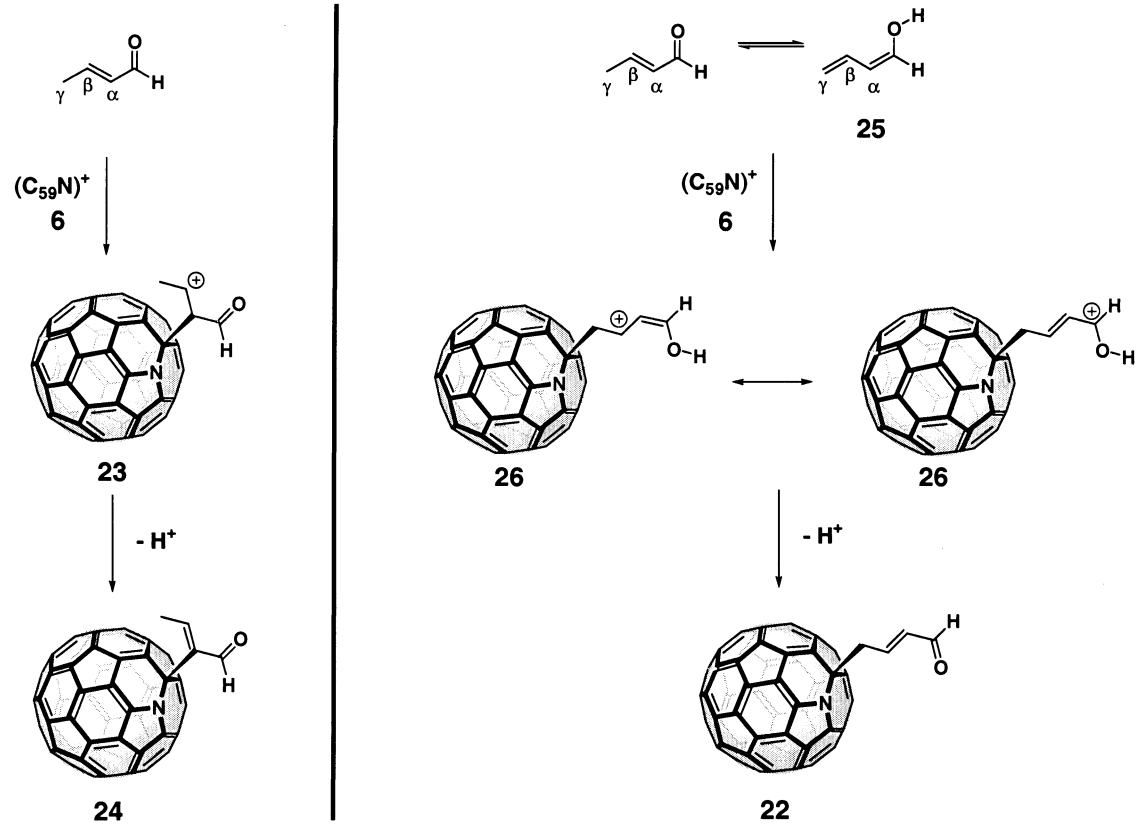


Scheme 11. Formation of 4-azafullerenyl-crotonaldehyde **22**.

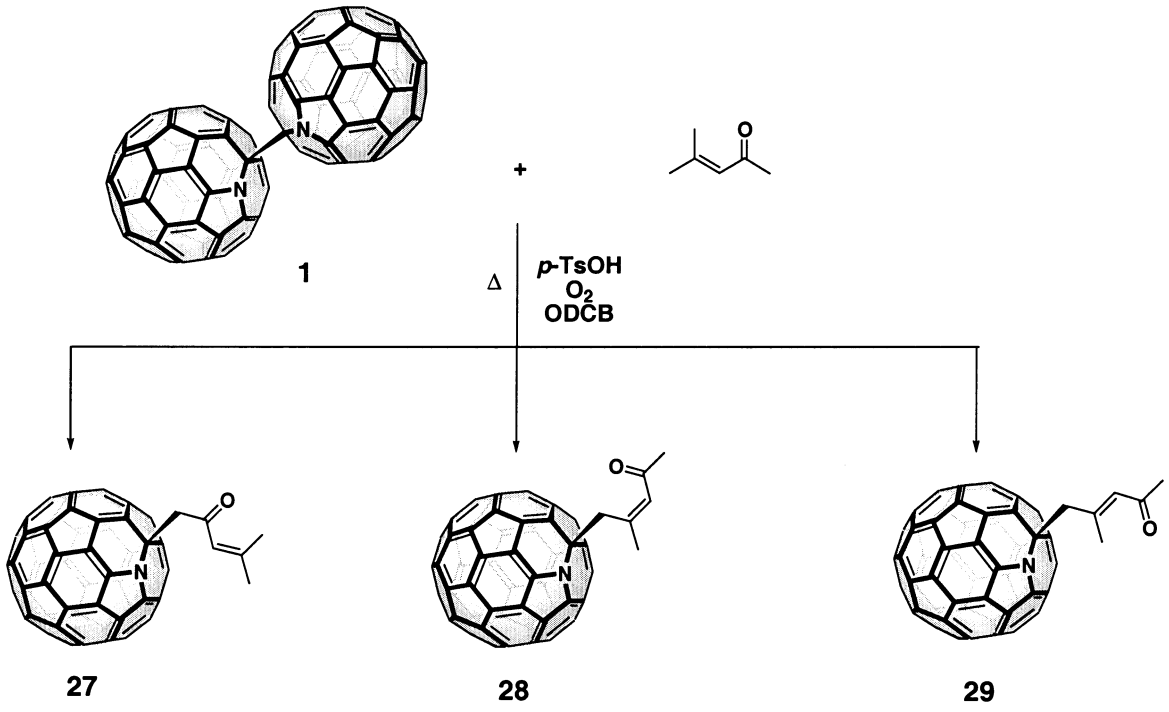
allyl-cation. Semiempirical calculations (PC Spartan Pro,[8] PM3) show that this cation is 14 kcal/mol more stable than cation **17**. Therefore, the attack of $C_{59}N^+$ (**6**) at one of the two possible positions in acetylacetone should be thermodynamically controlled, leading to the observed product **16**.

To show that sterical hindrance of the central methylene group is not too high, we used diethyl malonate as educt for the reaction. The treatment of **1** with 15 equiv. diethyl malonate in ODCB in the presence of 30 equiv. *p*-TsOH and air leads to the formation of two products, which can be isolated by flash chromatography on silica gel using toluene as eluent (Scheme 10).

The first fraction (R_f=0.7) is compound **20**. Here, a substitution of one of the two methylene protons of diethyl malonate by **6** takes place. The resonance of the remaining proton in the ^{1}H NMR spectrum appears at δ=5.6. Differentiation between the ^{13}C NMR signals of the methine group (δ=61.81) and the methylene group (δ=62.31) was achieved by DEPT NMR spectroscopy. The second product is ethyl (2-azafullerenyl)acetate (**21**) (R_f=0.5), formed by decarboxylation of compound **20** after partial saponification under the acidic conditions. In the ^{1}H NMR spectrum of **21** the signals of 2 equiv. methylene protons appear at δ=4.7. Both compounds are accessible in high purity. Compound **20** is slightly more soluble in organic solvents like ODCB or toluene than **21**. With longer reaction times the yield of **21** increases at the expense of **20**, indicating that the decarboxylation step takes place after the malonate addition to the heterofullerene. A reaction using ethyl acetate as educt does not yield any product at all. These experiments clearly demonstrate, that the stability of reaction intermediates caused by a conjugated π-electron system and not sterical effects determine the regioselectivity of the addition reactions with acetylacetone.



Scheme 12. γ versus α addition of **6** to crotonaldehyde.



Scheme 13. Reaction of **1** with mesityl oxide.

2.4. α,β-Unsaturated carbonyl compounds

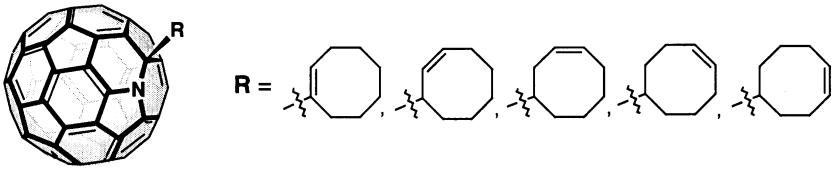
Treatment of **1** with 20 equiv. crotonaldehyde under the same reaction conditions as described above leads to the exclusive formation of compound **22** (R_f=0.6) (Scheme 11).

The ^{1}H NMR spectrum of **22** shows the signal of the aldehyde proton at δ=9.92 appearing as doublet, two different signals for the olefinic protons (δ=8.07, 6.91) and a doublet for the 2 equiv. protons of the methylene group (δ=4.79). The *E* configuration of the C–C double bond was determined by NOE NMR spectroscopy. The ^{13}C signals of the two olefinic carbon atoms (δ=147.26, 138.09) were identified by DEPT NMR spectroscopy. Hence, the reaction of crotonaldehyde with **1** can be described as a vinylogous substitution of a γ-proton by $C_{59}N^+$ (**6**). The preferred addition to the γ instead of the α position can also be explained with the thermodynamic stabilities of the intermediates **23** and **26** (Scheme 12).

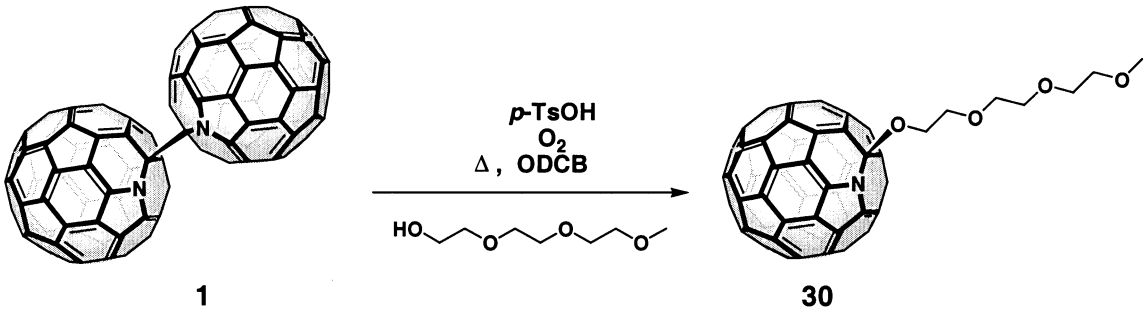
An attack of $C_{59}N^+$ (**6**) at the α-carbon atom of the non enolized crotonaldehyde leads to the formation of the intermediate cation **23**. This system is stabilized only by an +I-effect of the methyl group. After deprotonation compound **24** would be formed. When the attack of **6** takes place at the γ-position of crotonaldehyde, a donor stabilized allyl cation **26** is generated. For this process an acid catalyzed enolization to **25** has to be assumed. As shown with semiempirical calculations (PC Spartan Pro,[8] PM3), the allyl cation **26** is by about 20 kcal/mol more stable than **23**. Consequently, a thermodynamically controlled vinylogous attack, leading to the more stable intermediate **26**, is more favorable than an attack at the α-position. An attack to the α-carbon atom is unlikely due to its acceptor character.

Since **1** reacts with normal ketones at the α-position leading to α-azafullerenated ketones and with α,β-unsaturated carbonyl compounds to γ-substituted products, the question arises, which position is more reactive. To find out we used mesityl oxide as test compound, since it contains two methyl groups in the vinylogous position and one methyl group in α-position to the carbonyl function. Treatment of **1** with mesityl oxide leads to the formation of three different products (Scheme 13), which can be monitored by TLC (silica gel, toluene/ethyl acetate 9:1). The products were isolated by flash chromatography using toluene as eluent. The elution sequence is: **27** (R_f=0.93), **28** (R_f=0.85) and **29** (R_f=0.60) as the most polar fraction. The ^{1}H NMR spectra of all three compounds look very similar, showing three signals at about δ=4.6, 2.9 and 2.3, belonging to one methylene and two methyl groups. The structure assignment of **27**–**29** was carried out by NOE and DEPT spectroscopy.

The yield ratio of compounds **27**–**29** is about 1:1:1, showing



Scheme 14. Isomeric $C_{59}N$-cyclooctene adducts.



Scheme 15. Formation of methoxy-ethoxy-ethoxy-ethoxy-hydroazafulleren **30**.

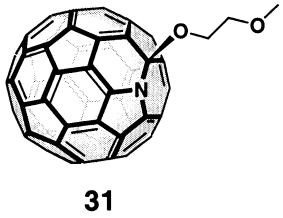


Figure 1.

that the reactivity of an α-position is approximately the same as that of a vinylogous position.

2.5. Other nucleophiles

In addition to reactions with carbonyl compounds we also tested whether the intermediate **6** can also be trapped with other nucleophiles. First we used cyclooctene. Treatment of **1** with this olefin under nearly the same conditions as described before leads to a compound mixture in high yield, containing at least three products as detected by HPLC (Cosmosil Buckyprep, toluene as eluent). The reaction is very fast and all compounds elute together as the least polar fraction on silica gel using toluene as eluent. It was not possible to obtain any compound in a pure form, not even by HPLC separation using a Cosmosil Buckyprep column. The EI-MS spectrum of the product mixture only shows a peak at *m/z* 861, corresponding to the M^+ peak of a cyclooctene-$C_{59}N$ adduct, together with a strong fragmentation peak at *m/z* 722 for $C_{59}N^+$. The ^1H NMR spectrum of the mixture shows signals for three different olefinic protons at about $\delta=5$. We therefore assume that at least three isomers of $C_{59}N$-cyclooctene were formed by acid catalyzed double bond isomerization leading to the isomeric compounds shown in Scheme 14.

As a further nucleophilic trapping reagent for $C_{59}N^+$ (**6**) alcohols were chosen. In order to achieve products with sufficient solubility, we used triethylenglycol monomethylether as an example. In a smooth reaction the corresponding $C_{59}N$-alcohol adduct **30** was obtained and isolated by flash chromatography (R_f=0.3) in high purity (Scheme 15).

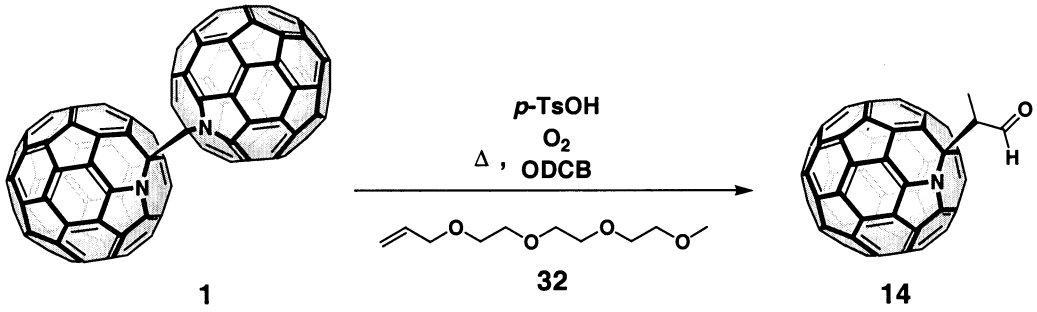
All monoazafullerene adducts described so far contained a carbon substituent at the sp^3-C-atom, which is adjacent to the nitrogen atom. The corresponding sp^3-C-atom in compound **30** is attached to an O-atom, forming an N,O-acetale. A similar compound **31** was observed as a by-product during the synthesis of **1** elaborated by our group (Fig. 1).[9]

The physical properties of this type of adduct are different from other monoazaheterofullerene derivatives mentioned above. In toluene, **30** forms a red-green solution in contrast to the olive-green solutions of other $C_{59}N$ adducts. Due to the attachment of an O-atom, the signal of the sp^3 cage C-atom of compound **30** is shifted about 20 ppm downfield in the ^{13}C NMR spectrum as compared to normal azaheterofullerene derivatives. The ^1H NMR spectrum shows the expected signals for the polyether side chain. The signals for the six methylene groups appear in the region at $\delta=3.4$–5.0 and the signal for the methyl group appears at $\delta=3.36$.

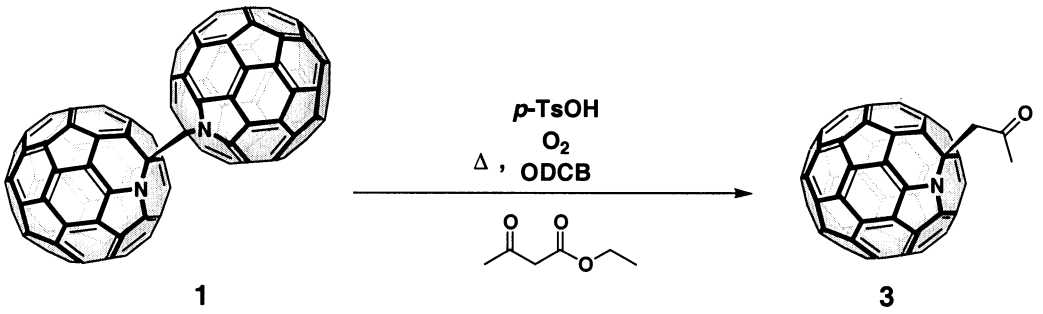
Regarding the fact, that the reaction of $(C_{59}N)_2$ (**1**) with alcohols leads to the formation of an N,O-acetal, an acidic cleavage of this acetal forming a cage-opened fullerene system should be possible. Experiments in this direction are the subject of our current research.

2.6. Other oxidizing reagents

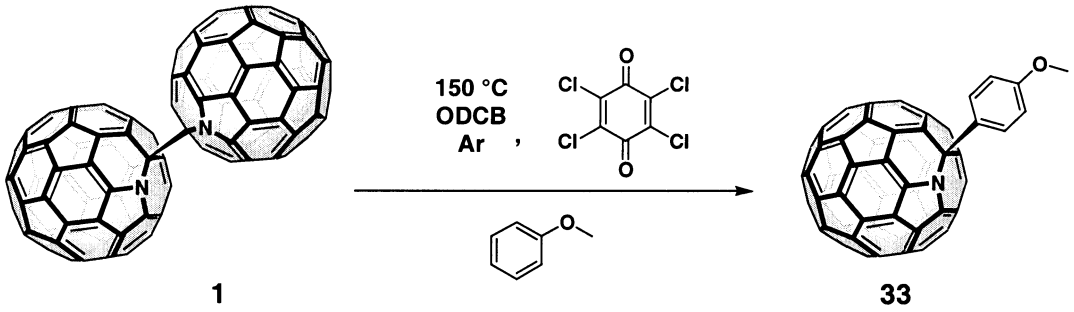
All reactions described so far were carried with molecular



Scheme 16. Reaction of **1** with an allylether leading to **14**.



Scheme 17. Reaction of **1** with ehtylacetoacetate leading to **3**.



Scheme 18. Oxidation with chloranil leading to **33**.

oxygen as oxidizing agent and they required the use of *p*-TsOH. The presence of an acid in the reaction mixture, however, can be a disadvantage in some cases. For example, the reaction with the allylpolyether **32** leads to the formation of 2-azafullerenyl-propanal (**14**) instead of the expected adduct (Scheme 16).

The acid effects the cleavage of the polyether, forming an allylalcohol, which subsequently isomerizes to a propionaldehyde under acid catalysis. It is unclear, whether this step takes place at the stage of an $C_{59}N$-olefin adduct intermediate or prior to the reaction with the heterofullerene.

A similar problem arises when ethyl acetoacetate is used as a trapping reagent. The only product isolated in this case is 1-azafullerenyl-propan-2-one **3** (Scheme 17).

Here, an acid catalized ester cleavage followed by a decarboxylation step takes place. It could not be determined at which stage this process happens. In addition, other nucleophiles like amines can not be used in the presence of an acid due to the formation of ammonium ions. Therefore, the corresponding $C_{59}N$ derivatives are not accessible in this way.

We therefore tried to generate $C_{59}N^+$ (**6**) by using other oxidizing agents. Treatment of $(C_{59}N)_2$ (**1**) with anisole in the presence of chloranil at 150°C under an argon atmosphere leads to the formation of the corresponding $C_{59}N$-anisole adduct **33**. The same adduct can also be obtained by using oxygen as oxidizing agent (Scheme 18).[6]

This demonstrates that chloranil is also able to oxidize the $C_{59}N$ radical (**2**) to the cation (**6**). The yield of the adduct formation, however, is lower than in the case of oxygen and *p*-TsOH. The high reaction temperature is unfavorable for the quinone system and causes degradation. The search for alternative oxidizing agents, e.g. ferrocenium hexafluorophosphate, is the subject of our current work.

3. Experimental

3.1. General remarks and materials

$(C_{59}N)_2$ was prepared according to literature procedures.[1] ^1H and ^{13}C NMR spectra were obtained from JEOL JNM EX and JEOL JNM GX instruments. Mass spectral data were obtained on a Varian MAT 311 a mass spectrometer. UV–VIS spectra were recorded on a Shimadzu UV-3102 spectrometer. IR spectra were obtained on a Bruker Vektor 22 instrument. HPLC analyses have been carried out on a Cosmosil Buckyprep Waters column (250×4.6 mm) using toluene as eluent.

3.2. General experimental procedure

30 mg (20.83 μmol) $(C_{59}N)_2$ and *p*-TsOH are dissolved in 100 ml ODCB. The nucleophilic compound is added to this solution. The reaction mixture is heated to 150°C while passing a constant stream of air through the solution until all of the $(C_{59}N)_2$ has been converted to the corresponding $C_{59}N$-adduct. The reaction can be monitored by TLC (silica gel, toluene/ethyl acetate 9:1). Afterwards the formed product is isolated by flash chromatography using toluene as eluent. The product is precipitated from CS_2/pentane, washed three times with pentane and dried in high vacuum.

3.2.1. *p*-Methoxy-ethoxy-ethoxy-ethoxy-hydroazafulleren 9. 50 equiv. methoxy-ethoxy-ethoxy-ethoxy-benzene,

20 equiv. *p*-TsOH, 4 h, 82% yield, R_f (silica gel, toluene/ethyl acetate 7:3): 0.46. IR (KBr): ν (cm^{-1})=2916, 2866, 1606, 1507, 1421, 1251, 1178, 1108, 578, 523; UV–Vis (CH_2Cl_2): λ_{max} (nm)=257, 320, 445, 589, 724; MS (EI): *m/z* 961 (M^+), 722 ($C_{59}N^+$); ^{1}H NMR (400 MHz, CS_2–20% $CDCl_3$): δ=8.69 (m, 2H), 7.34 (m, 2H), 4.30 (m, 2H; CH_2), 3.94 (m, 2H; CH_2), 3.73 (m, 2H; CH_2), 3.67 (m, 2H; CH_2), 3.62 (m, 2H; CH_2), 3.51 (m, 2H; CH_2), 3.35 (s, 3H; CH_3); ^{13}C NMR (100.5 MHz, CS_2–20% $CDCl_3$): δ=159.62 (1C; C-$(CH)_2$-OR), 154.08, 148.60, 147.54, 147.39, 147.36, 147.03, 147.00, 146.73, 146.37, 146.15, 145.99, 145.62, 145.42, 144.80, 144.32, 144.07, 143.76, 142.90, 142.52, 141.86, 141.57, 141.31, 141.20, 140.76, 140.65, 139.57, 137.29, 133.01, 132.69, 128.41 (2C; C-CHCOR), 123.86, 115.62 (2C; C-COR), 82.30 (1C; sp^3), 71.85 (1C; CH_2), 70.84 (1C; CH_2), 70.64 (1C; CH_2), 70.48 (1C; CH_2), 69.53 (1C; CH_2), 67.48 (1C; CH_2), 58.49 (1C; CH_3).

3.2.2. 1-Azafullerenylpropan-2-one 10. 20 equiv. acetone, 40 equiv. *p*-TsOH, 15 min, 96% yield, R_f (silica gel, toluene/ethyl acetate 9:1): 1.00. IR (KBr): ν (cm^{-1})= 2920, 2850, 1729, 1550, 1422, 1358, 1185, 1166, 578, 524; UV–VIS (CH_2Cl_2): λ_{max} (nm)=257, 320, 445, 589, 724; MS (EI): *m/z* 772 (M^+), 722 ($C_{59}N^+$); ^{1}H NMR (400 MHz, CS_2–20% $CDCl_3$): δ=4.91 (s, 2H; CH_2), 2.79 (s, 3H; CH_3); ^{13}C NMR (100.5 MHz, CS_2–20% $CDCl_3$): δ=201.80 (1C; C=O), 154.94, 148.31, 147.37, 147.11, 146.90, 146.38, 146.31, 146.02, 145.75, 145.50, 144.90, 144.74, 144.14, 143.79, 142.89, 142.54, 141.88, 141.56, 141.22, 141.01, 140.83, 140.78, 139.43, 137.41, 137.35, 127.26, 124.63, 78.37 (1C; sp^3), 53.84 (1C; CH_2), 30.90 (1C; CH_3).

3.2.3. 1-Azafullerenyl-2-phenylethan-2-one 11. 20 equiv. acetophenone, 40 equiv. *p*-TsOH, 15 min, 92% yield, R_f (silica gel, toluene/ethyl acetate 9:1): 1.00. IR (KBr): ν (cm^{-1})=2921, 2851, 1692, 1550, 1446, 1422, 1215, 1175, 1092, 577, 524; UV–VIS (CH_2Cl_2): λ_{max} (nm)=257, 320, 445, 589, 724; MS (EI): *m/z* 841 (M^+), 722 ($C_{59}N^+$); ^{1}H NMR (400 MHz, CS_2–20% $CDCl_3$): δ=8.40 (m, 2H), 7.74 (m, 1H), 7.70 (m, 2H), 5.45 (s, 2H; CH_2); ^{13}C NMR (100.5 MHz, CS_2–20% $CDCl_3$): δ=193.80 (1C; C=O), 155.02, 148.57, 147.57, 147.36, 147.10, 146.93, 146.87, 146.34, 146.26, 145.97, 145.73, 145.55, 145.44, 144.85, 144.71, 144.09, 143.77, 142.85, 142.54, 141.83, 141.53, 141.18, 141.03, 140.80, 140.75, 139.39, 137.42, 136.58, 134.93 (1C; *i*-Ar), 133.50 (1C; *p*-Ar), 128.76 (2C; Ar), 128.23 (2C; Ar), 124.78, 78.59 (1C; sp^3), 49.45 (1C, CH_2).

3.2.4. 2-Azafullerenylpropanal 14 and *E*-4-azafullerenyl-2-methylpent-2-enal 15. 45 equiv. propionaldehyde, 90 equiv. *p*-TsOH, 15 min, HPLC purification, R_f (silica gel, toluene/ethyl acetate 9:1): 1.00.

*Compound **14**:* IR (KBr): ν (cm^{-1})=2950, 2921, 1728, 1508, 1446, 1422, 1238, 1185, 990, 577, 555, 524; UV–Vis (CH_2Cl_2): λ_{max} (nm)=257, 320, 445, 589, 724; MS (EI): *m/z* 772 (M^+), 722 ($C_{59}N^+$); ^{1}H NMR (400 MHz, CS_2–20% $CDCl_3$): δ=11.07 (d, 1H, *J*=1.46 Hz; CHO), 4.63 (dq, 1H, *J*=1.46, 7.08 Hz; CH), 2.50 (d, 3H, *J*=7.08 Hz; CH_3); ^{13}C NMR (100.5 MHz, CS_2–20% $CDCl_3$): δ=198.79 (1C; CHO), 155.19, 149.50, 147.54, 147.32, 147.13, 146.88, 146.41, 146.28, 145.62, 145.58, 144.90, 144.74, 144.30, 143.76, 142.95, 142.60, 142.29, 141.94, 141.56, 141.28, 140.83, 140.71, 139.51, 137.26, 133.94, 133.74, 123.96, 85.14 (1C; sp^3), 56.98 (1C; CH), 10.11 (1C; CH_3).

*Compound **15**:* IR (KBr): ν (cm^{-1})=2950, 2921, 1726, 1686, 1508, 1446, 1422, 1317, 1238, 1185, 990, 577, 555, 524; UV–Vis (CH_2Cl_2): λ_{max} (nm)=257, 320, 445, 589, 724; MS (EI): *m/z* 819 (M^+), 722 ($C_{59}N^+$); ^{1}H NMR (400 MHz, CS_2–20% $CDCl_3$): δ=9.81 (s, 1H; CHO), 7.68 (dq, 1H, ^4J=1.46 Hz, *J*=10.1 Hz; =CH), 5.00 (dq, 1H, *J*=10.1, 6.84 Hz; CH), 2.50 (d, 3H, *J*=6.84 Hz; CH_3), 2.40 (d, 3H, ^4J=1.46 Hz; CH_3); ^{13}C NMR (100.5 MHz, CS_2–20% $CDCl_3$): δ=192.52 (1C; CHO), 155.25, 149.77, 147.60, 147.38, 147.28, 147.23, 146.98, 146.72, 146.35, 146.12, 145.67, 144.96, 144.76, 144.21, 143.76, 142.99, 142.77, 142.64, 141.97, 141.60, 141.33, 140.87, 140.80, 139.54, 137.31, 133.78, 130.20, 127.26, 124.01, 85.19 (1C; sp^3), 45.59 (1C; CH), 15.43 (1C; CH_3), 10.11 (1C; CH_3).

3.2.5. 1-Azafullerenyl-2,4-pentanedione 16. 15 equiv. acetylacetone, 20 equiv. *p*-TsOH, 20 min, 89% yield, R_f (silica gel, toluene/ethyl acetate 9:1): 0.95. IR (KBr): ν (cm^{-1})=2924, 2853, 1600, 1447, 1421, 1321, 1236, 1194, 577, 542, 523; UV–VIS (CH_2Cl_2): λ_{max} (nm)=257, 320, 445, 589, 724; MS (EI): *m/z* 821 (M^+), 722 ($C_{59}N^+$); ^{1}H NMR (400 MHz, CS_2–20% $CDCl_3$): δ=15.76 (s, 1H; O–H–O), 6.21 (s, 1H; =CH), 4.72 (s, 2H; CH_2), 2.27 (s, 3H, CH_3); ^{13}C NMR (100.5 MHz, CS_2–20% $CDCl_3$): δ=190.46 (1C; C=O), 188.59 (1C; C=O), 154.74, 148.33, 147.65, 147.34, 147.18, 146.92, 146.44, 146.33, 146.08, 145.71, 145.53, 144.95, 144.78, 144.25, 144.16, 143.83, 142.94, 142.61, 141.91, 141.60, 141.27, 141.09, 140.84, 140.76, 139.48, 137.38, 133.87, 124.30, 102.01 (1C, =CH), 79.32 (1C; sp^3), 50.84 (1C; CH_2), 24.47 (1C; CH_3).

3.2.6. Diethyl 2-azafullerenylmalonate 20. 15 equiv. malonic acid, 30 equiv. *p*-TsOH, 30 min, 49% yield, R_f (silica gel, toluene/ethyl acetate 9:1): 0.70. IR (KBr): ν (cm^{-1})=2974, 2925, 1735, 1551, 1460, 1424, 1365, 1186, 1093, 1016, 579, 524; UV–Vis (CH_2Cl_2): λ_{max} (nm)=257, 320, 445, 589, 724; MS (EI): *m/z* 821 (M^+), 722 ($C_{59}N^+$); ^{1}H NMR (400 MHz, CS_2–20% $CDCl_3$): δ=5.56 (s, 1H; CH), 4.56 (m, 2H; CH_2), 1.51 (t, 3H; CH_3); ^{13}C NMR (100.5 MHz, CS_2–20% $CDCl_3$): δ=165.40 (2C; C=O), 155.06, 147.49, 147.28, 147.07, 146.96, 146.73, 146.25, 146.16, 145.93, 145.66, 145.50, 145.44, 144.84, 144.62, 144.06, 143.71, 142.88, 142.57, 141.91, 141.65, 141.19, 140.78, 140.59, 139.04, 137.19, 134.86, 124.72, 79.35 (1C; sp^3), 62.31 (1C; CH_2), 64.81 (1C; CH).

3.2.7. Ethyl (2-azafullerenyl)acetate 21. 15 equiv. malonic acid, 30 equiv. *p*-TsOH, 30 min, 49% yield, R_f (silica gel, toluene/ethyl acetate 9:1): 0.50. IR (KBr): ν (cm^{-1})=2972, 2951, 2921, 2850, 1737, 1551, 1459, 1439, 1423, 1366, 1343, 1188, 1093, 1022, 579, 556, 525; UV–Vis (CH_2Cl_2): λ_{max} (nm)=257, 320, 445, 589, 724; MS (EI): *m/z* 821 (M^+), 722 ($C_{59}N^+$); ^{1}H NMR (400 MHz, CS_2–20% $CDCl_3$): δ=4.75 (s, 1H; CH_2), 4.55 (q, 2H; CH_2), 1.55 (t, 3H; CH_3); ^{13}C NMR (100.5 MHz, CS_2–20% $CDCl_3$): δ=168.29 (1C; C=O), 154.87, 148.04, 147.60,

147.32, 147.16, 147.05, 146.84, 146.40, 146.32, 146.05, 145.70, 145.62, 145.52, 144.91, 144.76, 144.20, 144.14, 143.82, 142.92, 142.60, 141.91, 141.60, 141.27, 140.96, 140.84, 140.78, 139.46, 137.38, 134.16, 124.37, 78.35 (1C; sp^3), 61.44 (1C; CH_2), 46.72(1C; CH_3).

3.2.8. 4-Azafullerenylcrotonaldehyde 22. 15 equiv. crotonaldehyde, 20 equiv. *p*-TsOH, 30 min, 71% yield, R_f (silica gel, toluene/ethyl acetate 9:1): 0.60. IR (KBr): ν (cm^{-1})=2935, 2922, 1691, 1550, 1508, 1423, 1363, 1185, 1175, 1093 1033, 765, 720, 577, 556, 529, 523; UV–Vis (CH_2Cl_2): λ_{max} (nm)=257, 321, 441, 554, 591, 719; MS (EI): *m/z* 791 (M^+), 722 ($C_{59}N^+$); ^{1}H NMR (400 MHz, CS_2–20% $CDCl_3$): δ=9.92 (d, 1H, *J*=7.57 Hz; CHO), 8.07 (m, 1H, *J*=7.57, 15.63 Hz; =CH), 6.91 (m, 1H, *J*=15.63, 7.57 Hz; =CH), 4.79 (d, 2H, *J*=7.57 Hz; CH_2); ^{13}C NMR (100.5 MHz, CS_2–20% $CDCl_3$): δ=164.81 (1C; C=O), 154.57, 147.60, 147.27 (1C; =CH), 147.19, 146.72, 146.48, 146.37, 146.13, 145.73, 145.66, 145.59, 144.98, 144.78, 144.38, 144.22, 143.80, 142.99, 142.64, 141.95, 141.55, 141.37, 140.98, 140.93, 140.74, 139.74, 138.09 (1C; =CH), 137.31, 133.60, 123.75, 80.89 (1C; sp^3), 46.42 (1C; CH_2).

3.2.9. 1-Azafullerenyl-4-methylpent-3-en-2-one 27. 15 equiv. mesityloxide, 20 equiv. *p*-TsOH, 45 min, 27% yield, R_f (silica gel, toluene/ethyl acetate 9:1): 0.93. IR (KBr): ν (cm^{-1})=2949, 2922, 2851, 1728, 1690, 1617, 1550, 1423, 1238, 1186, 1117, 1092, 1033, 766, 746, 529, 523; UV–Vis (CH_2Cl_2): λ_{max} (nm)=256, 322, 443, 589, 727; MS (EI): *m/z* 819 (M^+), 722 ($C_{59}N^+$); ^{1}H NMR (400 MHz, CS_2–20% $CDCl_3$): δ=6.72 (s, 1H; =CH), 4.87 (s, 2H; CH_2), 2.46 (s, 3H; CH_3), 2.16 (s, 3H; CH_3); ^{13}C NMR (100.5 MHz, CS_2–20% $CDCl_3$): δ=194.07 (1C; C=O), 158.10, 155.09, 148.93, 147.43, 147.12, 147.08, 147.03, 146.43, 146.32, 146.04, 145.79, 145.51, 144.91, 144.78, 144.14, 143.85, 142.90, 142.59, 141.88, 141.58, 141.20, 141.15, 140.82, 140.78, 139.41, 137.49, 134.31, 124.72, 123.68 (1C; =CH), 78.94 (1C; sp^3), 54.58 (1C; CH_2), 27.89 (1C; CH_3), 21.15 (1C; CH_3).

3.2.10. *Z*-5-Azafullerenyl-4-methylpent-3-en-2-one 28. 15 equiv. mesityloxide, 20 equiv. *p*-TsOH, 45 min, 22% yield, R_f (silica gel, toluene/ethyl acetate 9:1): 0.85. IR (KBr): ν (cm^{-1})=2950, 2921, 2851, 1685, 1617, 1559, 1550, 1423, 1239, 1197, 1186, 1176, 1094, 765, 580, 530, 524; UV–Vis (CH_2Cl_2): λ_{max} (nm)=257, 323, 446, 577, 730; MS (EI): *m/z* 819 (M^+), 722 ($C_{59}N^+$); ^{1}H NMR (400 MHz, CS_2–20% $CDCl_3$): δ=6.82 (s, 1H; =CH), 5.18 (s, 2H; CH_2), 2.78 (s, 3H; CH_3), 2.31 (s, 3H; CH_3); ^{13}C NMR (100.5 MHz, CS_2–20% $CDCl_3$): δ=196.60 (1C; C=O), 154.85, 149.88, 149.29, 147.65, 147.39, 147.32, 147.23, 147.07, 146.44, 146.28, 146.08, 145.71, 145.48, 144.91, 144.80, 144.32, 144.12, 143.85, 142.94, 142.55, 141.90, 141.62, 141.24, 140.76, 140.67, 139.39, 137.35, 133.29, 128.87 (1C; =CH), 124.26, 81.40 (1C; sp^3), 45.21 (1C, CH_2), 31.56 (1C; CH_3), 28.33 (1C; CH_3).

3.2.11. *E*-5-Azafullerenyl-4-methylpent-3-en-2-one 29. 15 equiv. mesityloxide, 20 equiv. *p*-TsOH, 45 min, 35% yield, R_f (silica gel, toluene/ethyl acetate 9:1): 0.60. IR (KBr): ν (cm^{-1})=2950, 2921, 2851, 1690, 1617, 1550, 1423, 1239, 1186, 1095, 1027, 963, 765, 530, 524; UV–Vis (CH_2Cl_2): λ_{max} (nm)=257, 319, 442, 556, 717; MS (EI): *m/z* 819 (M^+), 722 ($C_{59}N^+$); ^{1}H NMR (400 MHz, CS_2–20% $CDCl_3$): δ=6.94 (s, 1H; =CH), 4.59 (s, 2H; CH_2), 2.92 (s, 3H; CH_3), 2.35 (s, 3H; CH_3); ^{13}C NMR (100.5 MHz, CS_2–20% $CDCl_3$): δ=196.36 (1C; C=O), 154.67, 149.39, 148.55, 147.69, 147.38, 147.28, 147.19, 146.88, 146.52, 146.39, 146.17, 145.79, 145.71, 145.60, 145.00, 144.84, 144.36, 144.22, 143.85, 142.99, 142.66, 141.97, 141.60, 141.35, 141.15, 140.85, 140.74, 139.61, 137.35, 133.44, 129.86 (1C; =CH), 123.97, 81.51 (1C; sp^3), 54.31 (1C; CH_2), 31.57 (1C; CH_3), 22.59 (1C; CH_3).

3.2.12. Isomeric C_{59}N-cyclooctene-adducts. 50 equiv. Cyclooctene, 20 equiv. *p*-TsOH, 10 min, 91% yield of isomeric compounds, R_f (silica gel, toluene/ethyl acetate 9:1): 1.00. MS (EI): *m/z* 831 (M^+), 722 ($C_{59}N$).

3.2.13. Methoxy-ethoxy-ethoxy-ethoxy-hydroazafullerene 30. 50 equiv. triethylenglycol, 20 equiv. *p*-TsOH, 1 h, 43% yield, R_f (silica gel, toluene/ethyl acetate 9:1): 0.30. IR (KBr): ν (cm^{-1})=2921, 2865, 1585, 1550, 1439, 1423, 1239, 1196, 1184, 1146, 1096, 1022, 575, 524; UV–VIS (CH_2Cl_2): λ_{max} (nm)=260, 324, 436, 687, 762; MS (EI): *m/z* 885 (M^+), 722 ($C_{59}N^+$); ^{1}H NMR (400 MHz, CS_2–20% $CDCl_3$): δ=4.99 (m, 2H; =CH_2), 4.23 (m, 2H; CH_2), 3.90 (m, 2H; CH_2), 3.76 (m, 2H; CH_2), 3.68 (m, 2H; CH_2), 3.54 (m, 2H; CH_2), 3.36 (s, 3H; CH_3); ^{13}C NMR (100.5 MHz, CS_2–20% $CDCl_3$): δ=153.49, 146.93, 146.87, 146.66, 146.61, 145.67, 145.50, 145.20, 145.11, 145.05, 144.59, 144.40, 144.30, 143.77, 143.55, 142.91, 142.56, 142.41, 141.91, 141.81, 141.18, 141.03, 140.83, 140.63, 139.14, 136.53, 135.17, 124.92, 100.30 (1C; sp^3), 71.89 (1C; CH_2), 71.02 (1C; CH_2), 70.73 (1C; CH_2), 70.53 (1C; CH_2), 70.25 (1C; CH_2), 65.62 (1C; CH_2), 58.60 (1C; CH_3).

3.2.14. *p*-Methoxyphenylhydroazafullerene 33. $(C_{59}N)_2$ (15 mg, 10.41 μmol) is dissolved in 20 ml dry ODCB. The solution is degassed to remove any traces of oxygen. To the argon saturated solution 8 ml anisole and 215 mg (25 equiv.) chloranil are added. The reaction mixture is heated to 150°C while passing a constant stream of argon through the solution until all of the $(C_{59}N)_2$ has been converted to the corresponding C_{59}N-anisol adduct. The reaction can be monitored by HPLC (Cosmosil Buckyprep, toluene). Afterwards the formed product is isolated by flash chromatography using toluene as eluent. The product is precipitated from CS_2/pentane, washed three times with pentane and dried in high vacuum. *p*-Methoxyphenylhydroazafullerene is obtained in 29% yield.

3.3. Spectral data

See Ref. 2.

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