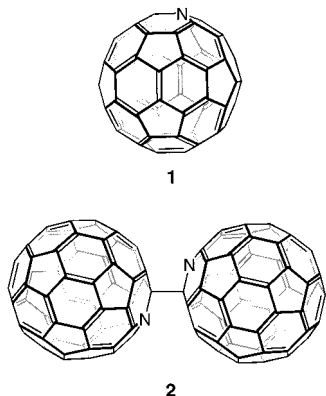# Nitrogen Heterofullerenes

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Introduction

Since the discovery of the bulk production of fullerenes,[1] synthetic chemists have been fascinated by the idea of developing chemical modifications of the all-carbon cages.[2] Apart from exohedral and endohedral fullerene derivatives, heterofullerenes[3] represent the third fundamental group of modified fullerenes and, as yet, the least explored one. In heterofullerenes, one or more carbon atoms of the cage are substituted by heteroatoms, such as the trivalent nitrogen or boron atoms. In these cases, substitution of an odd number of C atoms leads to radicals which can be stabilized by dimerization, whereas the replacement of an even number of C atoms would lead directly to closed-shell systems. The simplest representatives of nitrogen heterofullerenes, which are the subject of this Account, are aza[60]fullerene $C_{59}N$ (**1**) and its dimer, $(C_{59}N)_2$ (**2**).

1

2

Conceptually, the systematic substitution of cage C atoms by heteroatoms represents the three-dimensional counterpart of the transition of planar aromatics to hetereoaromatics, involving the same gain in structural and functional qualities. This is clearly an exciting per-

spective, since the isocyclic fullerenes alone exhibit a number of fascinating and, in many cases, unprecedented chemical, physical, and material properties.[2] Before 1995, experimental evidence for the existence of heterofullerenes was very rare. For example, in 1991, Smalley and co-workers[4,5] reported on the mass spectrometric detection of borafullerenes $C_{60-n}B_n$ ($n = 1-6$) generated by laser vaporization of graphite/boron nitride composites. Later, in the same year, the preparation of a number of C_nN_m clusters was reported.[6−8] However, none of these species has been isolated or structurally characterized. In 1994, Clemmer et al. presented evidence for heterofullerenes containing a metal as part of the framework.[9] They generated the ions NbC_n^+ ($n = 28-50$) by pulsed laser vaporization of mixed NbC/graphite rods under the condition of a quadrupole mass spectrometer. The experiments indicated that the detected masses for even n were due to endohedral fullerenes $Nb@C_n$, whereas clusters containing an odd number of carbons were rationalized as niobium heterofullerenes. Muhr et al. reported on the preparation of monoborafullerenes; however, presumably due to the instability of these systems, no pure material could be isolated and completely characterized.[10] The real preparative heterofullerene chemistry began in 1995. In that year, the exohedral fullerene chemistry reached a mature state, and many methods for the controlled addition of one or several addends to the fullerene framework had been developed.[2] At that time, it was discovered by the group of Mattay[11] and ourselves[12] that certain epiminofullerenes and azahomofullerenes (azafulleroids) are suitable precursors for the formation of positively charged heterofullerenes, such as $C_{59}N^+$ and $C_{69}N^+$ in the gas phase. Soon thereafter, the group of Wudl[13] and ourselves[14] published the first syntheses of azafullerenes. With these discoveries, heterofullerene chemistry as a new discipline within the area of fullerene research began. The first comprehensive review on heterofullerenes was published recently by Hummelen, Bellavia-Lund, and Wudl.[3] This excellent and detailed contribution covers almost the whole contemporary literature. In this Account we focus on our personal nitrogen heterofullerene story, starting with the first theoretical structure and property predictions in 1992. We will repeatedly point to the close relation of our work with that of the Wudl group, including the impact of Maurizio Prato and Kees Hummelen. This synergetic interaction was a most important driving force for the development of preparative heterofullerene chemistry.

Early Efforts

In 1992, when we were looking at the principles of the exohedral addition chemistry of C_{60} and C_{70} by investigating the first isomerically pure hydrofullerene derivatives,[15,16] we got in contact with the theoretician Heinrich Karfunkel from Ciba Geigy. We discussed the possibility of making heterofullerenes based on variations of the existing Krätschmer−Huffman method[1] for the production of fullerenes. Based on thermodynamic calculations, we
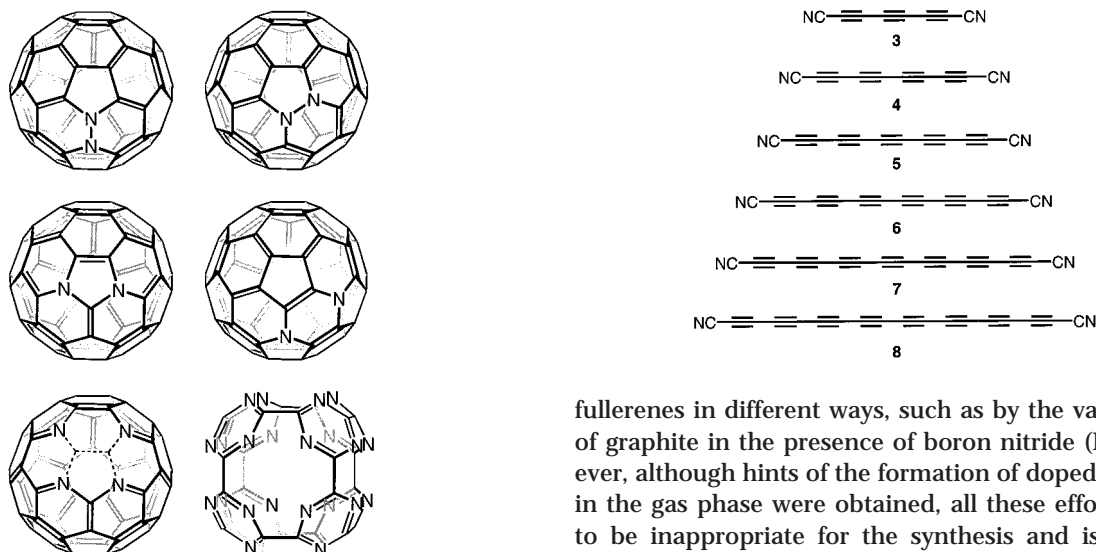
Andreas Hirsch was born in Esslingen, Germany, in 1960 and received his Ph.D. degree in 1990 from the University of Tübingen. Following postdoctoral studies at the Institute of Polymers and Organic Solids at UCSB from 1990 to 1991, he was research associate at the Institute of Organic Chemistry at the University of Tübingen. After his habilitation in 1994, he joined the faculty of the Department of Chemistry at the University of Karlsruhe as professor of organic chemistry (March 1995). Since October 1995, he is professor of organic chemistry at the University of Erlangen—Nürnberg.

Berthold Nuber was born in Nürtingen, Germany, in 1968. He studied chemistry at the universities of Tübingen and Karlsruhe, where he got his Diploma in 1995. He obtained his Ph.D. degree from the University of Erlangen—Nürnberg in 1998. Currently he is research associate at New York University.

FIGURE 1. Examples of quantum mechanically calculated bisaza-[60]fullerenes $C_{58}N_2$ and truncated azafullerenes.[17]

believed that the most promising possibility would be to use cyanogen $(CN)_2$ as nitrogen source, which could be incorporated into a hot precursor cluster during the formation of fullerenes from condensing C atoms to give nitrogen heterofullerenes. These experiments were thought to be easy to carry out, since we had just built a benchtop generator which allowed us to make our own fullerenes. The cyanogen was supposed to be injected directly during the vaporization of graphite or produced in situ using metal cyanide graphite composite target rods instead of pure graphite rods. These ideas were published together with a series of theoretical calculations on the structural, electronic, and thermochemical properties of possible heterofullerenes, such as several isomers of $C_{58}N_2$, or truncated heterofullerenes, such as $C_{54}N_4$ or $C_{24}N_{24}$.[17] Some examples of such systems are represented in Figure 1.
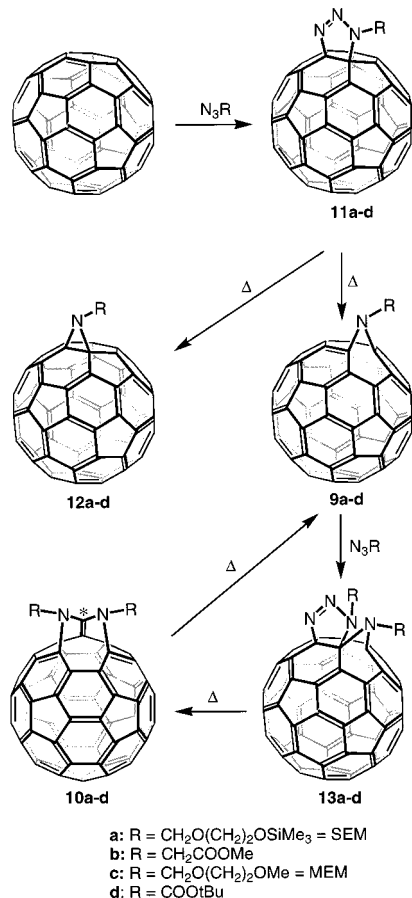
The calculations predicted such $C_{58}N_2$ isomers to be stable, closed-shell species and their geometries to be very similar to that of isocyclic C_{60}. Similar calculations were carried out later by Chen et al.[18] A faint resemblance of the truncated heterofullerenes to porphyrins or crown ether compounds is apparent (Figure 1). Indeed, it is predicted that some of those cluster-opened heterofullerenes are structurally and electronically similar to phthalocyanines and provide the same prerequisites for the complexation of central metals. However, when Thomas Grösser entered our group and tried to synthesize nitrogen heterofullerenes via the vaporization of graphite in the presence of cyanogen, we learned that no azafullerenes but rather the dicyanopolyynes **3**−**8** were formed, together with carbon soot.[19] These new carbon rods can be isolated by extraction with toluene and subsequent HPLC purification. They represent a homologous series of model compounds[20] for the linear carbon allotrope carbyne C_∞. The related monocyanopolyynes $H(C{\equiv}C)_nCN$ have been detected by Hare and Kroto as molecules in interstellar space.[21]

Later and partly in collaboration with Fred Wudl in Santa Barbara, Thomas Grösser tried to make hetero-

fullerenes in different ways, such as by the vaporization of graphite in the presence of boron nitride (BN). However, although hints of the formation of doped fullerenes in the gas phase were obtained, all these efforts proved to be inappropriate for the synthesis and isolation of heterofullerenes in bulk quantities. Until now, no heterofullerene directly formed by a modified Krätschmer−Huffman method has been isolated and completely characterized. If heterofullerenes are difficult to obtain via the direct vaporization of graphite in the presence of foreign molecules, is it then possible at all to gain access to this interesting class of molecules?
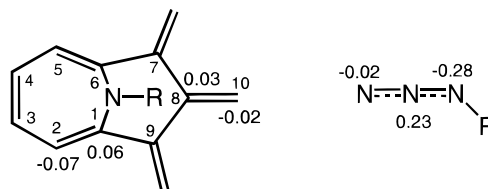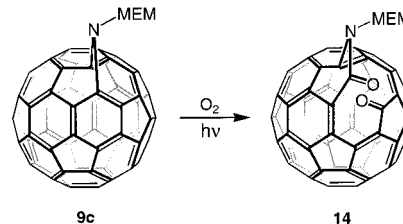
Nitrogen Heterofullerenes from Exohedral Imino Adducts of C_{60} and C_{70}

In the meantime, Maurizio Prato and Fred Wudl synthesized the first azafulleroid, **9a**, in which a cluster-opened [5,6] bond is bridged by an imino group (Scheme 1).[22] This azafulleroid was obtained together with another main product, **10a**, by the treatment of C_{60} with the corresponding alkyl azide in refluxing chlorobenzene. The other main product, **10a**, which converts to **9a** at temperatures >160 °C and whose structure could not be determined at that time, was not the expected triazoline intermediate **11a** formed by an initial [3 + 2] cycloaddition of the azide to a [6,6] double bond of the fullerene. Two years later, it was demonstrated by us via X-ray analysis of **11c** that the triazolines **11** are, indeed, the primary products in this reaction sequence.[23] For the synthesis and isolation of the triazoline, very concentrated solutions of the reactants, for example, in 1-chloronaphthalene, and moderate reaction temperatures, i.e., 60 °C, are required. At slightly higher temperatures, extrusion of N_2 takes place, leading to **9** and to the corresponding 1,2-epimino[60]fullerene **12**. In 1994, when Thomas Grösser investigated the regioselectivity of successive additions of stabilized nitrenes or alkyl azides to C_{60}, we found that, upon 2-fold reaction with methyl azidoacetate, a bisazafulleroid, **10b**, was formed with an extraordinary regioselectivity (Scheme 1).[24] Apart from this main product, only one other regioisomeric bisadduct was formed. Up to now, this bisazafulleroid formation is the most regioselective reaction in fullerene chemistry, neglecting tether-controlled additions. However, based on the spectroscopic evidence that we had at the time, we were not able to assign the structure of this bisazafulleroid. We just knew that it had

Scheme 1. [3 + 2] Cycloadditions of C_{60} with Azides and Follow-Up Reactions

a: R = $CH_2O(CH_2)_2OSiMe_3$ = SEM
b: R = CH_2COOMe
c: R = $CH_2O(CH_2)_2OMe$ = MEM
d: R = $COOtBu$

FIGURE 2. AM1 Mulliken charges near the imino bridge of **9b** and in N_3R (R = CH_2COOMe).[24]

Scheme 2. Reaction of Azahomo[60]fullerene 9c with Singlet Oxygen

C_s symmetry. With this unsolved problem, I (A.H.) went to Italy in October 1994 to participate at a fullerene meeting organized by the Italian Chemical Society, where Fred Wudl was awarded the Natta Medal. On the way to the meeting I visited Maurizio Prato in Padua, and I told him about the bisadduct. During the discussion, it turned out that our bisadduct **10b** had the same addition pattern as the original unidentified adduct **10a**. The spectroscopic properties of both compounds, especially the distinct ^{13}C NMR signal at $\delta = 160$ attributed to the central bridgehead C atom (marked with an asterisk), were almost identical. The structure of **10a** could not be identified in the first place, since no good mass spectra were obtained, and therefore it was not known that it was a bisadduct. On the other hand, Maurizio Prato and Vittorio Lucchini had the ^{13}C NMR spectrum of ^{15}N-labeled **10a**. With these collected data, it was now possible to assign the structure of **10a**. When Maurizio Prato and I subsequently traveled to Rome, we met Fred Wudl at the airport and told him about this discovery. Later, in a restaurant close to the Sistine Chapel, the three of us talked about further experiments in order to rationalize the very regioselective formation of **10**. We decided to look systematically at the remarkable reactivity of the [6,6] double bonds adjacent to the imino bridge.

Back in Tübingen, we could soon show that reaction of **9b** with methyl azidoacetate at room temperature leads only to one mixed triazoline/azafulleroid isomer, **13b**. As

corroborated by quantum mechanical calculations, the exclusive formation of **13b** is explained by the vinylamine character of the adjacent [6,6] bonds.[24] The significantly highest positive Mulliken charge of 0.06 (AM1) is located at C-1 and C-6, and the lowest of -0.07 at C-2 and C-5 (Figure 2). The most negatively polarized N atom of the azide is that bearing R. A kinetically controlled attack of the azide, therefore, leads predominantly to **13**. After extrusion of N_2 from **13**, the only possible regioisomeric bisadduct that can be formed without rearrangement is **10**. Later, Kees Hummelen and Fred Wudl showed that the vinylamine bond of **9** is also very susceptible to singlet oxygen.[25] The reaction afforded the first cluster-opened fullerene with a free orifice, namely the ketolactam **14**, which was formed presumably via an intermediate dioxetane (Scheme 2). Both cluster-modified derivatives **10** and **14** later turned out to be key intermediates for the first heterofullerene syntheses.

Before we describe the discovery of the heterofullerene formation from such activated precursor adducts, the development of alternative precursors and the syntheses of the corresponding C_{70} analogues are presented briefly. If instead of alkyl azides, nitrenes, formed, for example, by the thermal decomposition of azidoformates, are allowed to react with C_{60}, 1,2-epiminofullerenes such as **12** are formed as major products via [2 + 1] cycloadditions.[2] We have shown that 2-fold additions of nitrenes afford a mixture of all eight conceivable regioisomeric bisepimino[60]fullerenes.[26] In contrast to nucleophilic cyclopropanations of C_{60},[27,28] the *cis*-1 isomers **15**[29] are among the preferably formed regioisomers (Scheme 3, Figure 3). Significantly, in contrast to all other regioisomers, the *cis*-1 adducts **15** represented the first examples of fullerene adducts with open transannular [6,6] bonds.[26] This cluster-opening reaction, which proceeds via a retro-Diels−Alder process, is due to the combination of the *cis*-1 addition pattern and the presence of alkyloxycarbonyl substituents on the imino bridge. This allows for a favorable planarization of the imino bridge after ring opening, accompanied by the introduction of only three
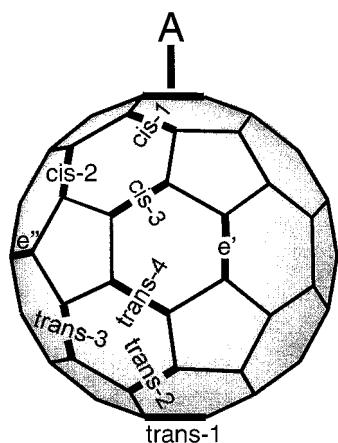
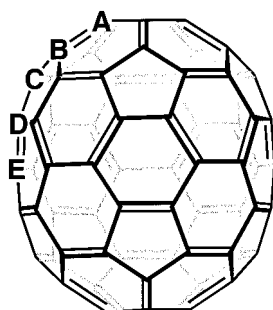**FIGURE 3.** Relative positional relationships of [6,6] bonds in a C_{60} derivative.
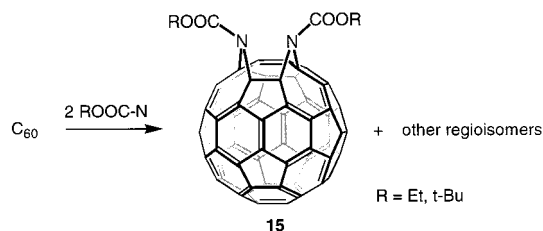

FIGURE 4. The five sets of different C atoms in C_{70}.

Scheme 3. Reaction of C_{60} with Nitrenes: Formation of *cis*-1 Adducts with Open Transannular [6,6] Bonds


unfavorable [5,6] double bonds. Indeed, acidic treatment of the BOC-protected **15** at elevated temperatures leads to the cluster-closed parent compound *cis*-1 $C_{60}(NH)_2$ (**16**), and subsequent reaction with ethyl chloroformate causes the fullerene cluster to reopen again.[30]

The regiochemistry of azide additions to C_{70} is more complicated since it has only D_{5h} symmetry and five sets (**A**−**E**) of topologically different C atoms (Figure 4). The most reactive bonds of C_{70} are the polar [6,6] bonds located between the C atoms of set **A** and set **B**.[31−33] The second most reactive are those between the C atoms of set **B**.

When we first investigated the regiochemistry of azide additions to C_{70}, we confirmed the expected behavior.[34] The treatment of C_{70} with methyl azidoacetate at moderate temperatures leads to the three regioisomeric triazolines **17**−**19** (Scheme 4) in a ratio of 12:3:1. This result was later confirmed in a study by Bellavia-Lund and Wudl, who investigated the system C_{70}/MEM-N_3.[35] Direct treatment of C_{70} with this azide at higher temperatures[34] or thermal

Scheme 4. Selective Thermal Extrusion of N_2 from Regioisomeric Triazolino[70]fullerenes
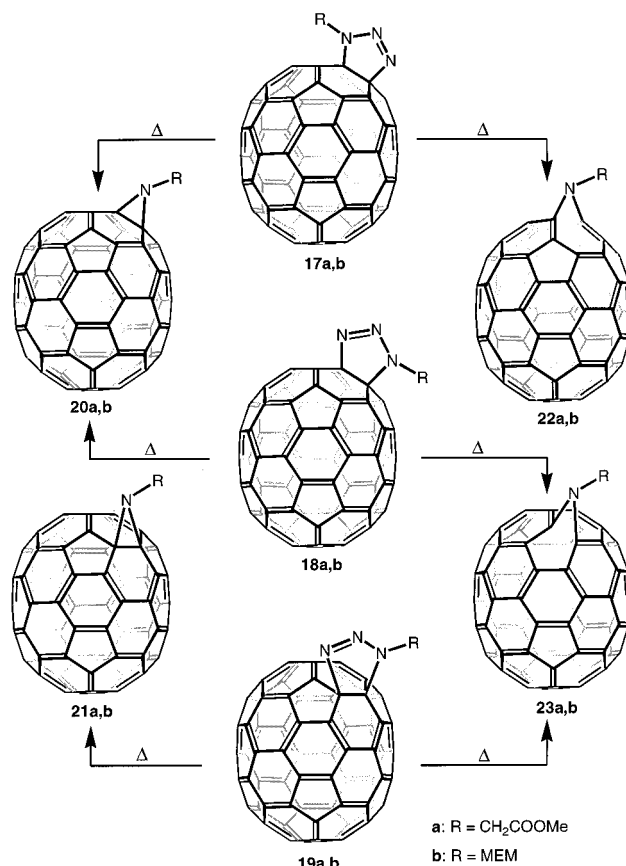
a: R = CH_2COOMe
b: R = MEM

decomposition of **17**−**19**[35] leads to the formation of the epimino[70]fullerenes **20**, **21** and the homoaza[70]fullerenes **22**, **23** (Scheme 4). It was shown that, upon nitrogen extrusion from the triazolines, no further rearrangements take place.[35] As in the case of C_{60}, bisazafulleroids are formed when the reaction with azides is carried out at 120 °C.[34] The two C_s-symmetric isomers **24** and **25**, with a 1,6;1,9- and 2,3;2,12-addition pattern, are formed in a ratio of 4:1 as the only regioisomers.
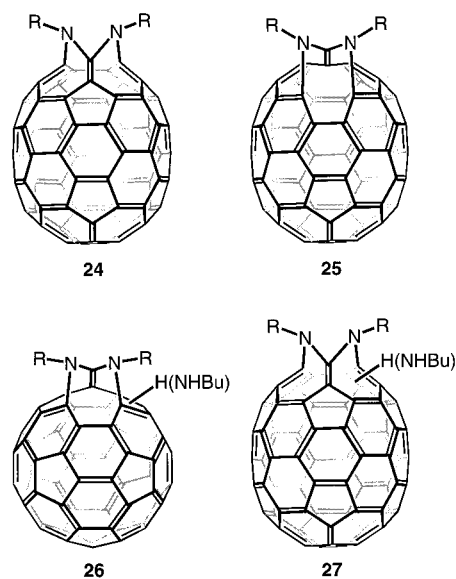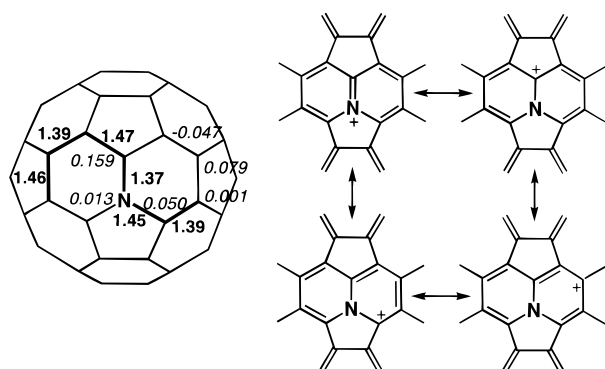
FIGURE 5. Characteristic bond lengths in angstroms (bold), Mulliken charges, and the most important resonance structures of $C_{59}N^+$.[12]

When we looked at the FAB mass spectra of cluster-opened **15** and the isomeric mixture of *n*-butylamine adducts **26** and **27**, we observed an unprecedented fragmentation behavior. Whereas usual exohedral adducts of C_{60} and C_{70} show the typical characteristics, namely relatively small M^+ peaks and the peaks of the fullerene fragment ions C_{60}^+ and C_{70}^+ at $m/z = 720$ or 840 as the most intense signals, the fragmentation of **15**, **26**, and **27** in the gas phase leads most efficiently to ions with masses of 722 or 842 amu.[12] We were able to prove very soon that these peaks are due to the heterofullerenium ions $C_{59}N^+$ and $C_{69}N^+$ since (1) after the first "shrink wrapping",[36] the signals of the fragment ions $C_{57}N^+$ and $C_{67}N^+$ are also of pronounced intensity (under these high-energy conditions, any exohedrally bound addends would be stripped off), (2) the ^{15}N-labeled analogues of **26** and **27** give rise to the most intensive fragmentation signals at $m/z = 723$ or 843, and (3) the high-resolution MS signals are consistent with the formulas $C_{59}N^+$ and $C_{69}N^+$. The parent ions $C_{59}N^+$ and $C_{69}N^+$ are isoelectronic with C_{60} and C_{70}. Semiempirical calculations show that $C_{59}N^+$ has almost the same structure as C_{60}, including the bond length alternation between the shorter [6,6] bonds and the longer [5,6] bonds[12] (Figure 5). The positive charge density is predominantly located in the neighborhood of the nitrogen substituent. Therefore, the resonance structures depicted in Figure 5 are the most important.

We thought for a while that we were the first who could make nitrogen heterofullerenes in the gas phase out of exohedral precursor adducts. But shortly after our discovery, we learned that, almost simultaneously, Mattay and co-workers[11] disclosed another route. They used the parent epimino[60]fullerene **28** as precursor adduct, which they generated via deprotection from the carbamate **12d** (R = COOtBu) (Scheme 5). The desorptive chemical ionization (DCI) mass spectrometry on **28** using ammonia as reagent gas afforded fragmentation signals at $m/z = 723$ and 724, which are due to $C_{59}NH^+$ and $C_{59}NH_2^+$. Ammonia as reagent gas played an important role, since using isobutane instead of NH_3 did not lead to the formation of heterofullerenes.

The forthcoming challenge was clear: One had to find a method for the bulk production of nitrogen heterofullerenes based on the mass spectrometric findings. When I (A.H.) presented our first results on the hetero-

Scheme 5. Synthesis of Epimino[60]fullerene 28 and Formation of Nitrogen Heterofullerenes in the Gas Phase by Desorptive Chemical Ionization (DCI) Mass Spectrometry
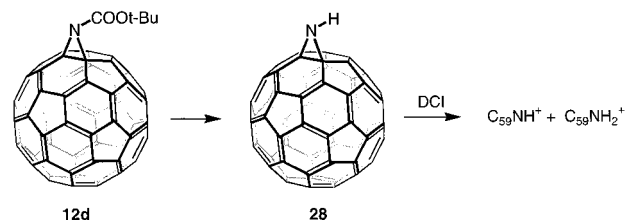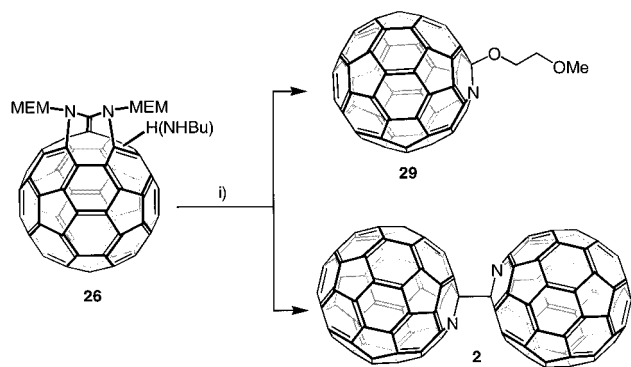

Scheme 6. Synthesis of the Aza[60]fullerene Dimer 2 Starting from the Cluster-Opened Ketolactam 14
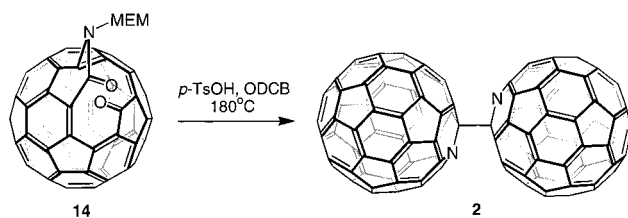
fullerene formation at a fullerene meeting in Varenna, Italy, Fred Wudl stood up and announced that his group had already made "$C_{59}N$" as the diamagnetic dimer **2** in bulk quantities. Their synthesis was based on the observation that the cluster-opened ketolactam **14** also efficiently fragments under FAB mass spectrometric conditions to $C_{59}N^+$. In this case, the fragmentation to C_{60} was not observed at all. Soon after this discovery, they found the right synthetic conditions to mimic the fragmentation events in the gas phase.[13] Refluxing cage-opened **14** in *o*-dichlorobenzene (ODCB) in the presence of a 12−20-fold excess of *p*-TsOH under an atmosphere of nitrogen leads to the formation of heterofullerene "$C_{59}N$", which exhibits a green color in solution (Scheme 6).

As demonstrated by a variety of techniques, including cyclic voltammetry and ESR and ^{13}C NMR spectroscopy, instead of **1**, which is an open-shell system, the diamagnetic dimer **2** was isolated. The suggested mechanism for the formation of **2** involves as a first step the acid-catalyzed cleavage of the MEM group, followed by an intramolecular ring formation to a 1,3-oxazetidinium system. This intermediate then loses formaldehyde and CO to form the azafulleronium ion $C_{59}N^+$, which is subsequently reduced to the $C_{59}N$ monomer (**1**). The reducing agent was proposed to be 2-methoxyethanol (the cleavage product of the MEM group) or water. In a final step, dimerization of **1** leads to $(C_{59}N)_2$ (**2**). This mechanism is supported by experiments in which the first cleavage product[29] was trapped, for example, by nucleophiles.[37] The monomer $C_{59}N$ (**1**) was later detected by us[38] and the Wudl group[39] via light-induced ESR measurements (LESR). Shortly after this first synthesis of heterofullerenes in bulk quantities, we elaborated our own method, which is based on the fragmentation of activated bisazafulleroids to $C_{59}N^+$ or $C_{69}N^+$ in the gas phase (Scheme 7).[14] The treatment of the bisazafulleroid **10** with *n*-butylamine and DBU in toluene and the subsequent reaction of the amine adduct **26** in the presence of 20 equiv of *p*-TsOH in refluxing ODCB in an argon atmo-

Scheme 7. Synthesis of Aza[60]fullerenes Starting from Activated Bisazafulleroids[a]
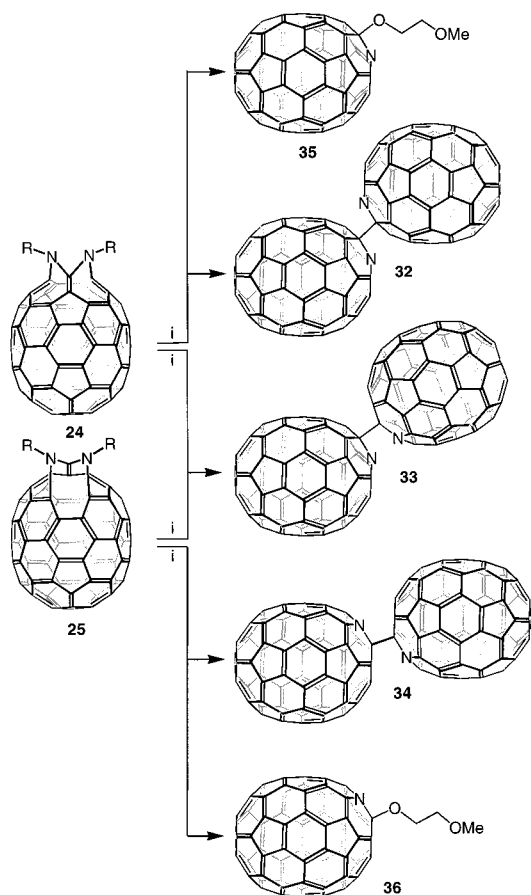

[a] Conditions: (i) *p*-TsOH, ODCB, heat.

Scheme 8. Synthesis of Aza[70]fullerenes Starting from Bisazafulleroids[a]

[a] Conditions: (i) *n*-butylamine, *p*-TsOH, ODCB, heat.

sphere leads to **2** in an optimized yield of 26%. Interestingly, together with the dimer **2**, the alkoxy-substituted monomeric compound **29** was formed. This exohedral heterofullerene adduct, however, is not stable in the long term in solution but decomposes to form a cluster-opened system exhibiting carbonyl vibrations in the IR spectra. Nevertheless, **29** was the first heterofullerene whose ^{13}C NMR spectrum shows the resonance for sp^3 fullerene C atoms at $\delta = 90.03$,[14] similar to those of the interfullerene bond within **2**.[40]

Although the mechanism of the fragmentation reaction is not fully understood at present, the following considerations seem reasonable. According to the regioselectivity principles pointed out earlier, the amine should add preferably to double bonds adjacent to the nitrogen bridges to form the adducts **30** and/or **31**. The central enediamine double bond turned out to be not accessible in a variety of addition reactions.[12,13] Both adducts **30** and **31** contain a BuN–C–N segment, which could give rise to an elimination of a carbodiimide moiety, BuN=C=NR. Removal of an isocyanide cleavage product is not likely, since running the reaction with the [5,6]-bridged monoadduct **9c** instead of **10c** does not cause the formation of any heterofullerenes. Mass spectrometric investigations clearly show that the nitrogen atom within the azafullerene framework must originate from one of the imino bridges of the bisazafulleroid precurso, since ^{15}N-doped **10b** afforded $C_{59}{}^{15}N^+$ (FAB-MS), despite the fact that undoped *n*-Bu^{14}NH$_2$ was used to activate the fullerene core.[12]
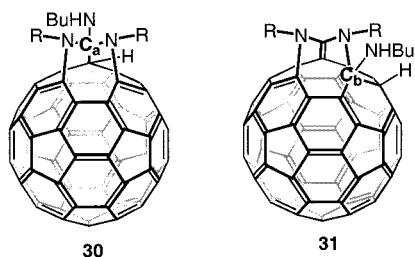

Similar to Wudl's synthesis, precursors bearing acid-labile groups are required, since, for example, the CH$_2$-COOMe-substituted bisazafulleroid **10b** does not lead to heterofullerenes under such synthetic conditions. Trapping the intermediate azafullerenonium ion with 2-meth-

oxymethanol (from cleavage of the MEM groups) explains the formation of **29**, whereas reduction to **1** and subsequent dimerization is the most likely pathway to **2**. Immediately after this success, we used the same method for the first synthesis of aza[70]fullerenes $(C_{69}N)_2$.[14] Considering the mechanistic investigations described above, the formation of different $(C_{69}N)_2$ isomers depending on the nature of the bisazafulleroid precursor is expected. Bisazafulleroid **24** is the precursor of aza[70]heterofullerenes, where a C atom of set **A** is replaced by a N atom, whereas **25** serves as starting material for heterofullerene isomers containing the N atom in the **B** position. When we allowed a 4:1 mixture of **24** and **25** to form heterofullerenes using our methodology, we obtained a mixture of all three possible dimers **32**–**34** involving **AA′**, **AB′**, and **BB′** substitution patterns (Scheme 8).

The ratio of the constitutional isomers **32**–**34** as determined by HPLC was 16:3:1. The fact that mixed dimers are also easily accessible reflects another aspect of the great diversity within heterofullerene chemistry. As in the case of the aza[60]fullerenes, alkoxy-substituted monomers **35** and **36** are formed together with the dimers **32**–**34** (Scheme 8).[14] These two monomers are formed in a ratio of 7:1. Also, for these higher heterospheres, ^{13}C NMR spectroscopy reveals a closed structure. For example, the signal of the sp^3 C atom of **35** appears at $\delta = 96.42$. In the meantime, the Wudl group also applied their method

Scheme 9. Synthesis of Aza[70]fullerenes Starting from Aza[70]fulleroids[a]

22 → (i) → **37** → (ii) → **32**

23 → (i) → **38** → (ii) → **34**
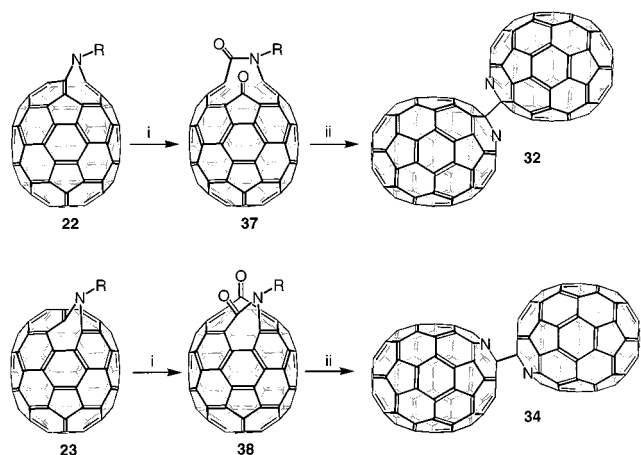
[a] Conditions: (i) $^1O_2$. (ii) *p*-TsOH, ODCB, heat.

of heterofullerene formation to the synthesis of aza[70]-fullerenes.[41] Starting from the [5,6]-bridged azahomo[70]-fullerenes **22** and **23**, they selectively synthesized the **AA′** isomer **32** and the **BB′** isomer **34** (Scheme 9).

More recently, evidence for the formation of the **CC′** isomer has been reported.[3] The Wudl group also synthesized the first mixed $C_{59}N/C_{69}N$ heterodimers.[3] Both the heterofullerene synthesis starting with a 1:1 mixture of the ketolactams **14** and **38** and the thermal treatment of $(C_{59}N)_2$ **2** with an equimolar amount of **AA′**-$(C_{69}N)_2$ **(32)** leads to the mixed products **39** and **40**, respectively. The product mixture of the latter reaction contained the homodimers, $(C_{59}N)_2$ **(2)** and $(C_{69}N)_2$ **(32)**, and the heterodimer **39** in a 1:1:2 ratio.

39

40

Chemistry of Azafullerenes

In addition to **29**, **35**, and **36**, a variety of additional derivatives formed during the formation of azafullerenes or from $(C_{59}N)_2$ **(2)** itself have been synthesized since the heterofullerene chemistry began. The heterofullerene transformation of the ketolactam **14** in the presence of a 15-fold excess of hydroquinone leads to the parent hydroaza[60]fullerene, **41**.[37] The hydroquinone is assumed to reduce the $C_{59}N$ radical intermediate (Scheme 10).

The length of the interdimer bond in $(C_{59}N)_2$ was calculated to be 160.9 pm (average C−C bond 154 pm),

Scheme 10. Synthesis of Hydroaza[60]fullerene 41

$\xrightarrow[\text{ODCB}]{\substack{p\text{-TsOH} \\ \text{hydroquinone}}}$

14 → **41**

Scheme 11. Synthesis of the Aza[60]fullerene Derivatives 42−44[a]

2

(i) / (ii) / (iii)

42 / **43a-d** / **44**

a: Ar = $C_6H_4CH_3$

b: Ar = $C_6H_4OCH_3$

c: Ar = ---⟨⟩—$O(CH_2)_2CHMe$

d: Ar =

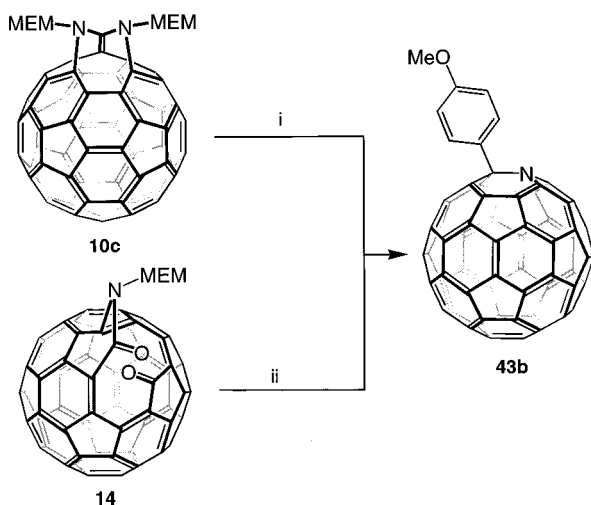[a] Conditions: (i) ODCB, air, *hν*. (ii) ArH, *p*-TsOH, air, reflux. (iii) CH₂Ph₂, air, reflux.

with a bond energy of only 18 kcal/mol.[42,43] Indeed, as already pointed out above, an easy homolytic cleavage of this bond can be achieved thermally or photochemically. The monomeric radical **1**, therefore, should offer a valuable synthetic potential. This was, indeed, demonstrated with the thermal treatment of **2** in ODCB in the presence of excess diphenylmethane (Scheme 11).[40] The resulting formation of **44** is consistent with a free radical chain mechanism. Interestingly, treatment of **2** with diphenylmethane under photolytic conditions does not produce **44**, but the *N*-oxide **42** (Scheme 11).

We elaborated another reaction sequence leading very efficiently to arylated heterofullerenes **43**.[44] The treatment of **2** with electron-rich aromatics in the presence of air and excess of *p*-TsOH leads to aza[60]fullerene derivatives **43** in yields up to 90% (Scheme 11). With anisole, toluene, and related aromatics, the para-substituted compounds were obtained exclusively, whereas arylation with 1-chlo-

Scheme 12. Formation of the Arylated Heterofullerene 43b from Bisazafulleroid and Ketolactam Precursors[a]

10c

14

43b

[a] Conditions: (i) *n*-butylamine, ODCB/anisole, *p*-TsOH, air, reflux. (ii) ODCB/anisole, *p*-TsOH, air, reflux.

Scheme 13. Synthesis of the Tetrachlorinated Compounds 45 Containing an Integral Pyrrole Moiety within the Fullerene Framework

43a-c

45a-c

a: Ar = $C_6H_4CH_3$
b: Ar = $C_6H_4OCH_3$
c: Ar = ···⬡—$O(CH_2)_2CHMe_2$

46 X = Cl, Br

ronaphthalene leads to the formation of various substitution products. The arylation with heteroaromatics such as thiophene also succeeded. The proposed mechanism of this reaction involves an electrophilic aromatic substitution by $C_{59}N^+$, which is presumed to be formed via thermal homolysis of the dimer, followed by oxidation of **1**. The oxidation is a critical step since running the reaction under argon does not yield arylated products. The reaction fails in the case of *N,N*-dimethylaniline (presumably due to deactivation caused by protonation of the amino group), as well as with deactivated aromatics such as ODCB, which is therefore the solvent of choice for this arylation. Interestingly, arylated azafullerenes are also accessible from the heterofullerene precursors **10** and **14** by thermal treatment in the presence of aromatics and air (Scheme 12). Although the yields are lower than those starting from **2**, one reaction step can be saved. On the other hand, if the reaction is carried out in 1-chloronaphthalene at 220 °C, **43d** is obtained in an isolated yield of 46%.

Since arylated aza[60]fullerenes are stable, exhibit favorable solubility properties, and are obtainable in high yields, they represent ideal starting materials for the investigation of the behavior of the $C_{59}N$ core toward addition reactions. As an example, we recently investigated the chlorination of **43a**−**c** with ICl in CS_2 at room temperature.[45] This reaction leads to the tetrachlorinated heterospheres **45a**−**c**, which were isolated as orange microcrystals in 50−60% yield (Scheme 13). The structures of **45a**−**c** were determined by ^{13}C NMR spectroscopy. They are closely related to the hexachlorides and hexabromides $C_{60}X_6$ (X = Cl, Br, **46**) previously described by Birkett et al.[46,47] In analogy to the cyclopentadiene subunit in **46**, the compounds **45** contain an integral pyrrole moiety decoupled from the conjugated π-system of the fullerene cage. The chlorine addends can be easily removed from the cage by treating **45** with an excess of PPh₃ at room temperature. The reversible binding could provide a useful strategy for protection of several double bonds of the fullerene core.
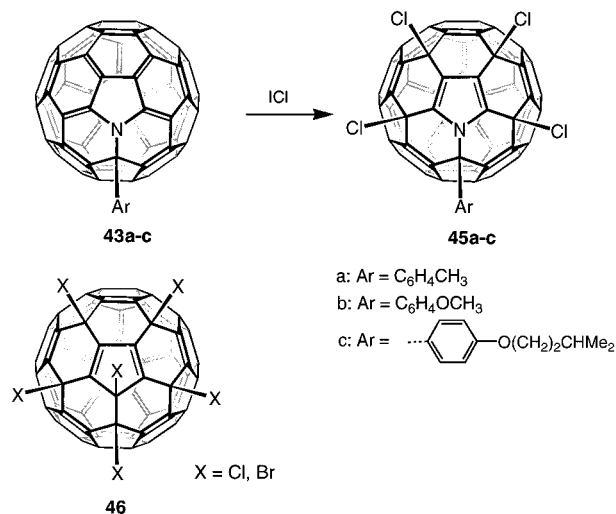
Conclusion

Heterofullerene chemistry is still a very young discipline within synthetic organic chemistry. So far, it is restricted to monoazafullerenes. However, looking at this first series of heterofullerene derivatives, it becomes clear how great the structural diversity of this compound class is. Preparative challenges for the future are, for example, syntheses of diazafullerenes $C_{58}N_2$ as stable diamagnetic monomers, syntheses of higher substituted azafullerenes $C_{60-n}N_n$, syntheses of heterofullerenes containing other elements, and syntheses of truncated heterofullerenes such as those represented in Figure 1. Since our knowledge of the physical and chemical behavior of these fascinating cage molecules and their derivatives is steadily increasing, it is just a question of time when these goals will be reached.

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