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Rearrangements to Cyanocyclopentadiene and Fulvenallene

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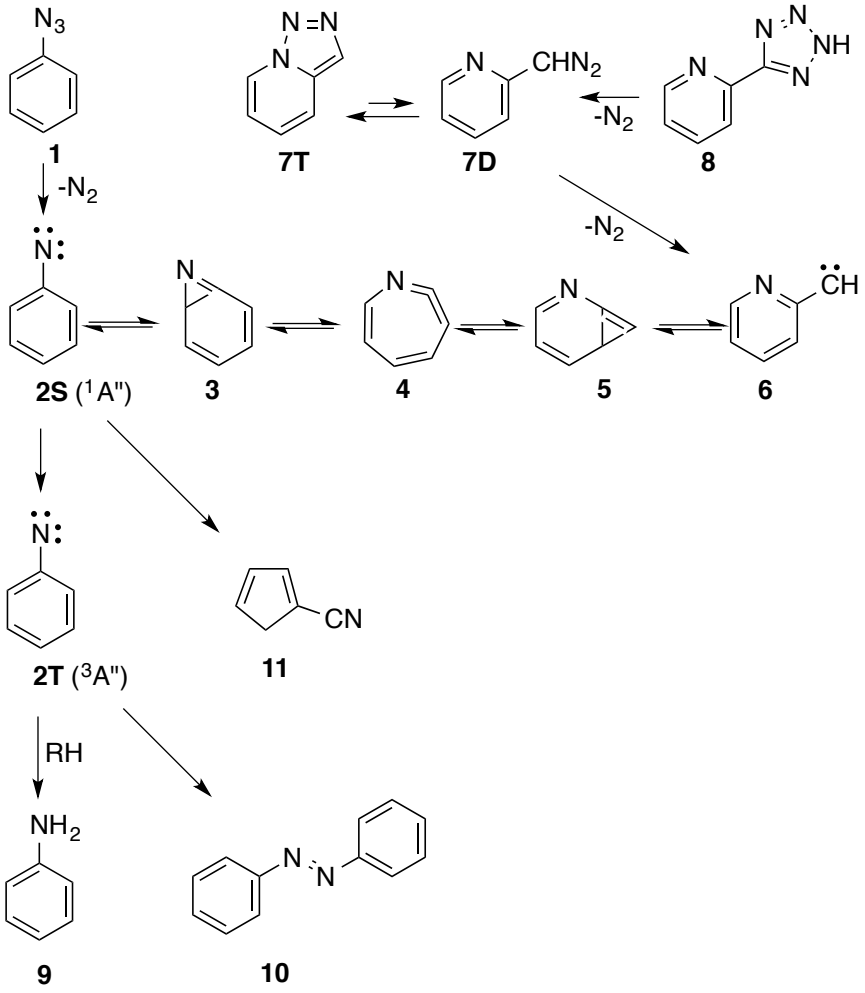
Abstract: Flash vacuum thermolysis (FVT) of phenyl azide **29** as well as precursors of 2-pyridylcarbene **34** and 4-pyridylcarbene **25** affords phenylnitrene **30** (labeled or unlabeled) as revealed by matrix-isolation ESR spectroscopy. FVT of 1-^{13}C-phenyl azide **29** affords 1-cyanocyclopentadiene (cpCN) **32**, which is exclusively labeled on the CN carbon, thus demonstrating direct ring contraction in phenylnitrene **30** without the intervention of cycloperambulation and 1,3-H shifts. However, the cpCN obtained by rearrangement of pyridyl-2-(^{13}C-carbene) **34** carries ^{13}C label on all carbon atoms, including the CN carbon. Calculations at the B3LYP/6-31G* level and in part at the CASSCF/6-31G* and CASPT2/cc-pVDZ//CASSCF(8,8)/cc-pVDZ levels support a new mechanism whereby 2-pyridylcarbene rearranges in part via 1-azacyclohepta-1,2,4,6-tetraene **36** to phenylnitrene, which then undergoes direct ring contraction to cpCN. Another portion of 2-pyridylcarbene undergoes ring expansion to 4-aza-cyclohepta-1,2,4,6-tetraene **42**, which then by trans-annular cyclization affords 6-azabicyclo[3.2.0]cyclohepta-1,3,5-triene **43**. Further rearrangement of **43** via the spiroazirine **44** and biradical/vinylnitrene **45** affords cpCN with the label on the CN group. An

analogous mechanisms accounts for the labeling pattern in fulvenallene **60** formed by ring contraction of 1-^{13}C-phenylcarbene **59** in the FVT of 1-^{13}C-phenyldiazomethane **58**.

Introduction

Phenyl azide **1** affords three principal products on flash vacuum thermolysis (FVT): aniline **9**, azobenzene **10**, and 1-cyanocyclopentadiene **11** (Scheme 1).[1] Compounds **9** and **10** are known to arise from the triplet ground state phenylnitrene **2T** (T_0, ^{3}A").[2] The rule of spin conservation[3] predicts that **11**, being a rearrangement product, arises from the singlet nitrene. The first excited singlet state **2S** lies 15-16 kcal/mol above the triplet and is an open-shell species (S_1, ^{1}A").[4]

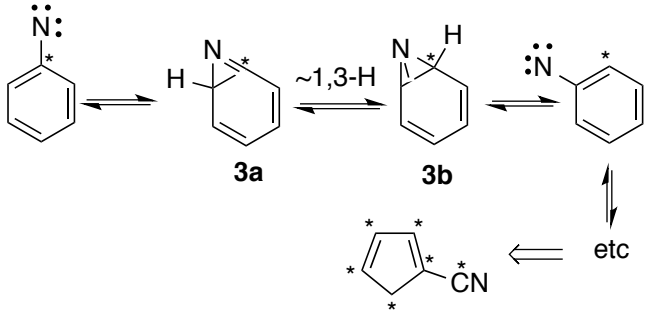


Scheme 1. Products of thermolysis of phenyl azide **1** and 2-diazomethylpyridine **7** and interconversion of phenylnitrene **2S** and 2-pyridylcarbene **6**. RH denotes any molecule from which **2T** may abstract hydrogen to yield aniline **9**.

Singlet phenylnitrene also undergoes rapid ring expansion to 1-aza-cyclohepta-1,2,4,6-tetraene **4** thermally[1d] and photochemically,[5] presumably via 7-aza-bicyclo[4.1.0]hepta-2,4,7-triene **3**. Furthermore, 2-pyridylcarbene **6** enters the same energy surface and affords the same products **9**-**11** when generated thermally.[1d,6] Using matrix isolation IR and ESR spectroscopy, Chapman, Sheridan and LeRoux have shown that both **2** and **6** undergo photochemical ring expansion to **4**, and the pyridylcarbenes and phenylnitrene interconvert photochemically.[7] The

thermal rearrangement of 2-pyridylcarbenes to phenylnitrenes has been demonstrated in several cases by direct observation of the ESR spectra of the nitrenes following FVT of the carbene precursors, viz. triazolo[1,5-*a*]pyridine **7T** or tetrazolylpyridine **8**, both of which generate the 2-diazomethylpyridine valence isomer **7D** as a transient intermediate.[8,9,10,11]

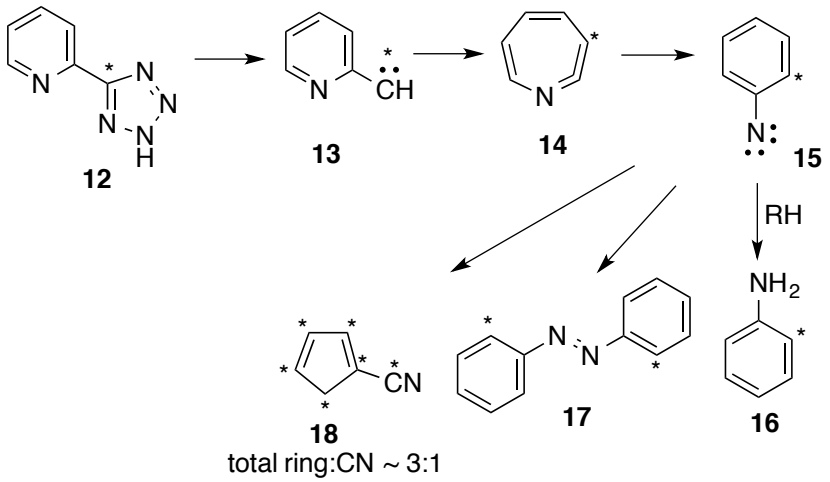
The mechanism of formation of cyanocyclopentadiene (cpCN) **11** has been an enigma for over 45 years. There have been three previous isotopic labeling studies. The first two,[12] using ^{14}C and ^{13}C labeling of phenyl azide, concluded that there was scrambling of all carbon atoms in phenyl nitrene prior to ring contraction, and this was proposed to take place via 1,3-hydrogen shifts in the bicyclo[4.1.0]heptatriene intermediates (**3a** ⇄ **3b**; the cycloperambulatory mechanism, Scheme 2). In this study, the position of the ^{13}C label was assayed by mass spectrometry only.[12b] It is well known that carbon scrambling takes place frequently in molecular ions.[13]



Scheme 2. The cycloperambulatory mechanism.[12] * = ^{13}C label

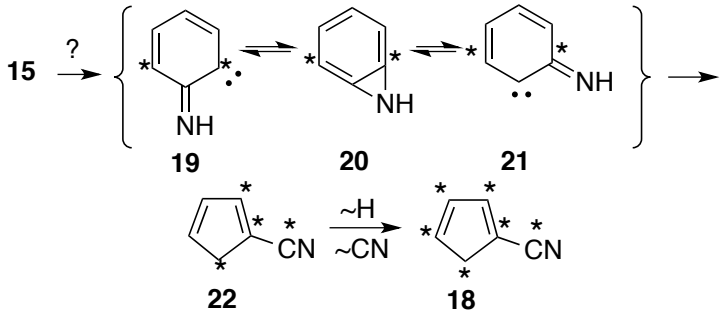
Our own labeling study used 2-(5-^{13}C-5-tetrazolyl)pyridine **12** (91 atom-% ^{13}C) as a precursor of ^{13}C-2-pyridylcarbene **13**.[14] The outcome of FVT was that aniline **16** and azobenzene **17** were labeled exclusively in the *ortho* positions, as expected from the rearrangement of **13** to **15** (Scheme 3 and Figure S1, Supporting Information). However, cpCN **18** was labeled on all

carbon atoms, including the CN group, with a total ring/CN ratio of ca. 3:1 (Figure S2, Supporting Information).



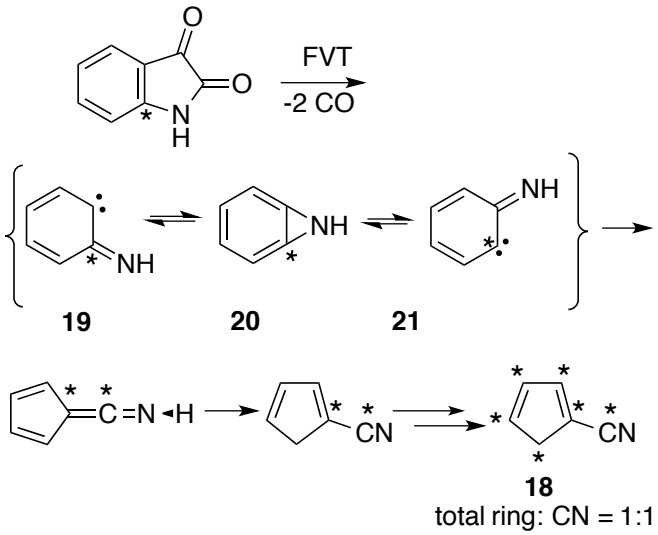
Scheme 3. Observed products derived from the 2-pyridylcarbene – phenylnitrene rearrangement.

To explain this unexpected scrambling result, formation and interconversion of the iminocarbenes and benzazirine **19-21** prior to ring contraction to cpCN **22** was postulated (Scheme 4).[14] Rapid thermal 1,5-shifts of H and CN with calculated activation barriers of the order of 25-34 kcal/mol would equilibrate the ring labels over the five ring-carbons,[1e] and these 1,5-shifts would be accelerated by chemical activation arising from the exothermicity of the ring contraction reaction.[1e]



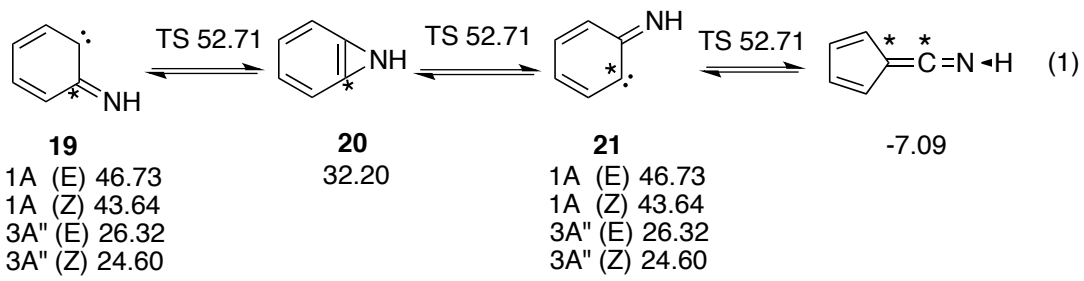
Scheme 4. Potential but non-applicable rearrangement of phenylnitrene to iminocyclohexadienylidene.

The mechanism in Scheme 4 was based on the deceptive similarity with the ^{13}C labeling study of isatin, where interconversion of the iminocarbenes **19** and **21** via benzazirine **20** prior to ring contraction to cyanocyclopentadiene was clearly established (Scheme 5 and Figure S3, Supporting Information).[14]

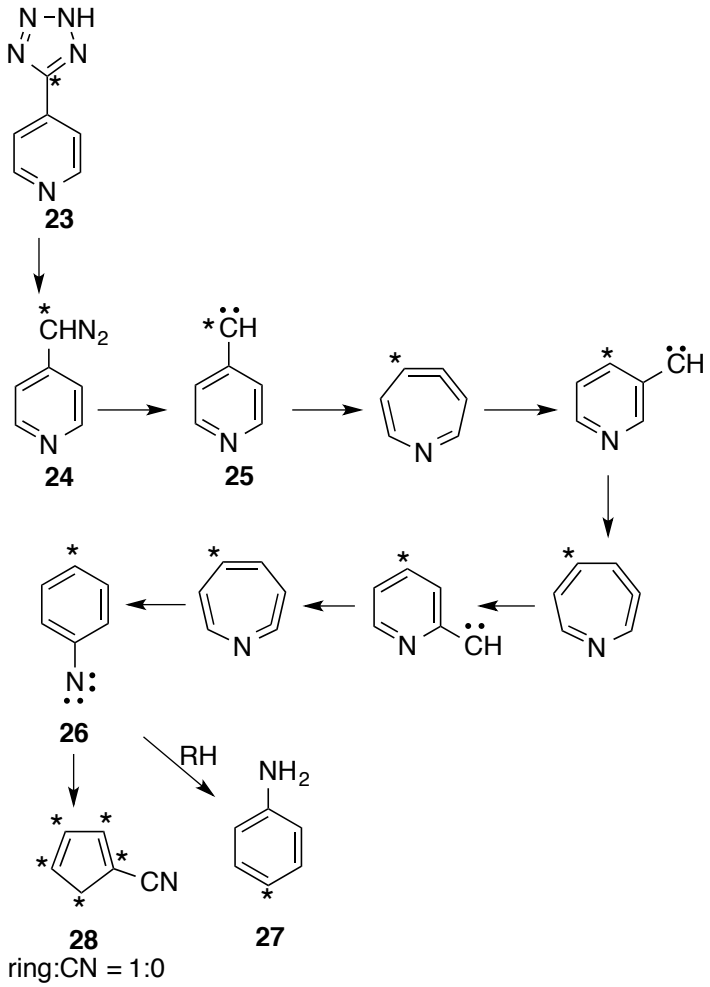


Scheme 5. The formation of ^{13}C-cyanocyclopentadiene from 7a-^{13}C-isatin at 715 ^{o}C/0.15 mbar.

This proposal is correct for the isatin reaction (Sheme 5), where the iminocarbene **19** is formed directly. Our calculations at the B3LYP/6-31G* + ZPVE level indicate that the closed-shell singlet carbenes **19** and **21** can interconvert easily through the lower-energy benzazirine **20**, with modest activation barriers (Eq. 1; energies in kcal/mol are relative to triplet phenylnitrene **2T** for ease of comparison with data discussed below).



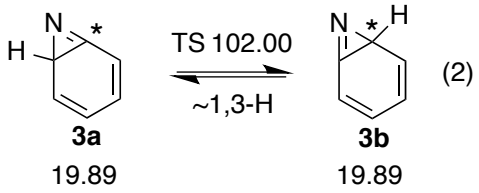
We have also reported that ^{13}C-4-pyridylcarbene **25**, generated by FVT of 4-(5-^{13}C-5-tetrazolyl)pyridine **23**, yielded aniline **27**, which was exclusively labeled in the *para* position, whereas the cyanocyclopentadiene **28** was labeled on all ring carbons but carried no detectable label on the CN group (Scheme 6).[14] Here too, rapid 1,5-shifts[1e] of H and CN scramble the ring label over the five ring positions, but the CN group remains unlabeled.



Scheme 6

This clear-cut result rules out the operation of the cycloperambulatory mechanism (Scheme 2) and the occurrence of any 1,3-H shifts in intermediates that can return to phenylnitrene. This is

not surprising, as thermal 1,3-shifts are expected to have very high activation barriers. In fact, our new calculations give an activation barrier of 82 kcal/mol for the reaction **3a** ⇄ **3b** (Eq. 2) (B3LYP/6-31G* energies + ZPVE in kcal/mol relative to phenylnitrene **1T**)



(2)

We now report a new ^{13}C labeling study, which puts the previous conclusions into jeopardy and reveals a radically new mechanism of ring contraction in arylcarbenes and arylnitrenes. There is no support for the mechanisms shown in Schemes 2 and 4 and Eq. 2.

Results and Discussion

1. Phenylnitrene. 1-Cyanocyclopentadiene **11** is obtained by FVT of phenyl azide **1**,[1a,b] but the reaction is not straightforward. Under the high-vacuum conditions normally employed in FVT, azobenzene **10** is by far the major product, usually accompanied by some aniline **9**, formed by H-abstraction from other molecules (Scheme 1). Very little if any cpCN **11** is formed under these conditions.[1d] The best conditions for obtaining cpCN is "violent pyrolysis" whereby the azide is distilled rapidly into the FVT tube maintained at 800 ^{o}C in a vacuum of ca. 10^{-3} mbar. The high concentration of azide vapor at the entrance to the hot tube creates a shock-wave, which propagates back into the sample flask, therefore causing all of the liquid azide to evaporate rapidly. The temperature of the sample flask rises to above 100 ^{o}C, the pressure in the hot tube increases to ca. 1 mbar, and a bluish gas is seen to pulsate through the apparatus – pulsating

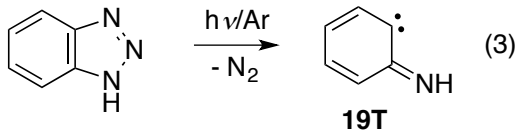
because the velocity of the gas exceeds the pumping speed. Attempts to measure the spectrum of the bluish emission at visible wavelengths have failed so far, but it is noted as an aside that the photolysis of aryl azides at cryogenic temperatures often produces blue or blue-green fluorescence or phosphorescence. The bluish gas carries the products into cold traps cooled in liquid-N_2, and cpCN can be isolated in yields up to 18% and purified by gas chromatography. The isolated cpCN should be stored at or below -20 ^oC to avoid dimerization. The high-pressure conditions of the FVT experiment also result in the formation of some aniline (usually not more than 10%).

We have also generated cpCN **11** by pulsed pyrolysis[15,16] of phenyl azide **1**. Here, phenyl azide vapor in Ar at a stagnation pressure of 1.7-2 atm is admitted through a pulsed valve to a high-temperature pyrolysis capillary in an assembly directly attached to a liquid-helium cryostat. The free jet expansion of the pyrolysate emanating from the capillary ensures rapid cooling of the products prior to isolation in an Ar matrix at ca. 10 K. An IR spectrum of cpCN **11** formed in this manner is shown in Figure S4, Supporting Information. CpCN is the major product, and at most traces of azobenzene are formed under these conditions. There was no evidence for the N-H absorptions of aniline in the 3400-3500 cm^{-1} region because most collisions will take place with Ar atoms rather than molecules RH.

The ESR spectrum of triplet phenylnitrene **2T** is obtained by isolating the product of FVT of phenyl azide **1** in an Ar matrix at 10-15 K in a cryostat for ESR spectroscopy (Figure S5).[8] The same ESR spectrum was obtained by Ar matrix photolysis of **1**,[17] or by FVT of triazolo[1,5-*a*]pyridine **7T** (Scheme 1) at 300 $^oC/10^{-3}$ mbar,[8] of 3-pyridyldiazomethane (obtained by FVT of 3-(5-tetrazolyl)pyridine) at 600 $^oC/10^{-4}$ mbar, or of 4-(5-tetrazolyl)pyridine and 4-(5-^{13}C-5-

tetrazolyl)pyridine **23** (Scheme 6) at 500 ^{o}C/10^{-4} mbar (Figures S5 and S6, Supporting Information).

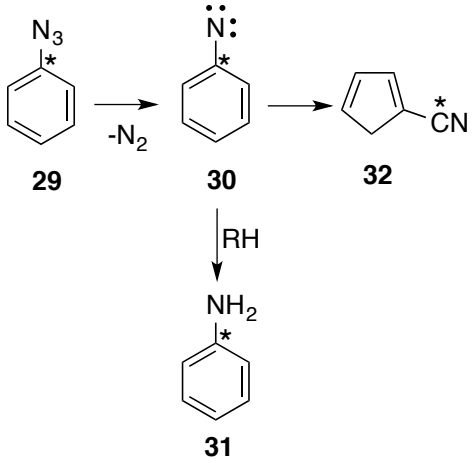
For comparison, the triplet iminocyclohexadienylidene/diradical **19T** (unlabeled) was generated by photolysis of benzotriazole in Ar matrix at 254 nm (Eq. 3); it is characterized by its strong H_{min} signal at 1318 G (H_0 = 3373.3 G), D/hc = 0.1704 cm^{-1} and E/hc = 0.0025 cm^{-1} as previously reported by Strauss et al. for the powder photolysis at 77 K.[18] These signals were not obtained on FVT of benzotriazole at 500 ^{o}C with Ar-matrix isolation of the product. The ESR signals of **19T** were not present in the product of either FVT or photolysis of phenyl azide **1**, and the signal of phenylnitrene **2T** was not present in the ESR spectra of either FVT (500 ^{o}C/10^{-4} mbar) or photolysis of benzotriazole in Ar matrixes. Thus, on the basis of ESR spectroscopy, there is no cross-over between phenylnitrene **2T** and iminocyclohexadienylidene **19T**.



19T (3)

2. 1-^{13}C-Phenylnitrene. 1-^{13}C-Phenyl azide **29** (90 atom-% ^{13}C) was prepared from 1-^{13}C-benzoic acid by Schmidt rearrangement to 1-^{13}C-aniline followed by diazotization and Sandmeyer reaction with sodium azide. FVT of this azide at 500 ^{o}C/10^{-3} mbar with Ar matrix isolation of the product at 15 K in a cryostat for ESR spectroscopy afforded the ESR spectrum of phenylnitrene **30** (D/hc = 0.990(5) cm^{-1}, E/hc = 0.000 cm^{-1}; Figure S5c, Supporting Information). A splitting due to coupling with the ^{13}C nucleus was not observed.

FVT of 1-^{13}C-Phenyl azide **29** under the conditions described above for "violent pyrolysis", viz. 800 ^{o}C (10^{-4} – 1 mbar) afforded cyanocyclopentadiene **32**, which was *exclusively labeled on the CN carbon*, as clearly determined by ^{13}C NMR spectroscopic comparison with unlabeled and labeled samples (Scheme 7). Only traces of azobenzene were formed under these conditions, and it was not assayed. Aniline **31** was formed and as expected labeled only at C1.

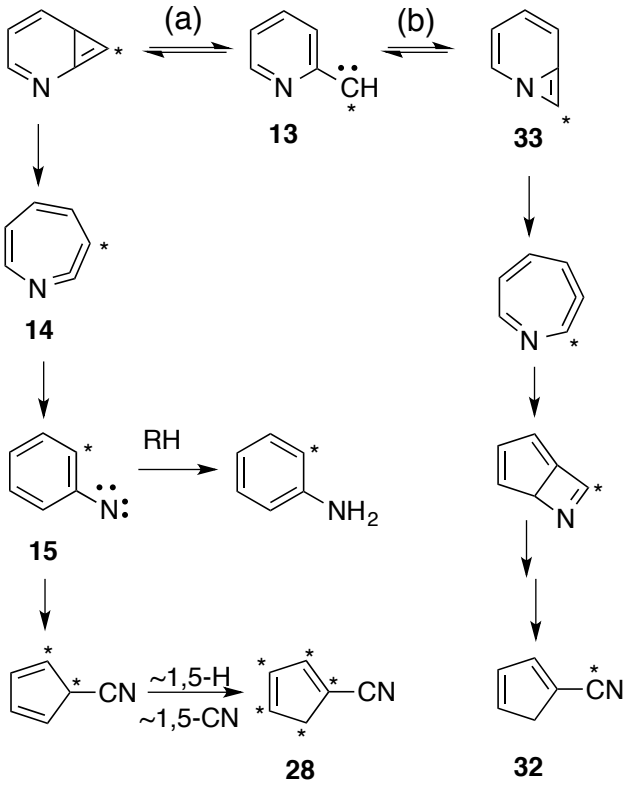


Scheme 7. Products of FVT of 1-^{13}C-phenyl azide. * = ^{13}C

These results demonstrate that the products **31** and **32** are formed from the unrearranged phenylnitrene **30**, an outcome which is incompatible with the previously proposed mechanisms (Schemes 2 and 4).[12,14]

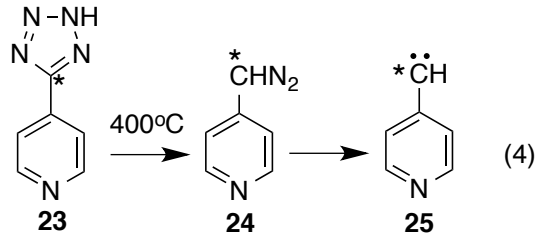
The combination of the new result (Scheme 7) with the ones obtained for ^{13}C-labeled 2-pyridylcarbene[14] (Scheme 3) demands that *2-pyridylcarbene undergoes ring contraction to cyanocyclopentadiene by a mechanism different from that of phenyl nitrene*. The rearrangement of the carbene to the nitrene is established without doubt (vide supra and Figures S5-S6, Supporting Information). Thus, a portion of 2-pyridylcarbene does rearrange to phenylnitrene and affords aniline, azobenzene, and cpCN by the *direct* ring contraction mechanism (Scheme 7).

Another portion of the 2-pyridylcarbene must undergo ring contraction to cpCN by a different mechanism. The logical way for 2-pyridylcarbene to do this is to cyclize onto the N atom to form an azirine **33** (Scheme 8). The CN moiety in **33** will eventually become the CN group in **32**. The sum of the two pathways a and b (Scheme 8) for ^{13}C-2-pyridylcarbene leads to cyanocyclopentadiene labeled in the ring (**28**) as well as on the CN group (**32**), as required. The new mechanism incorporates a nitrene route (route a) and a carbene route (route b), whereby route a is favored over route b by a factor of ~3. Further details are provided in Scheme 9 and discussed in Section 4 below. The carbene route borrows from the mechanism we have established previously for phenylcarbene,[19] which will be discussed in Section 5.



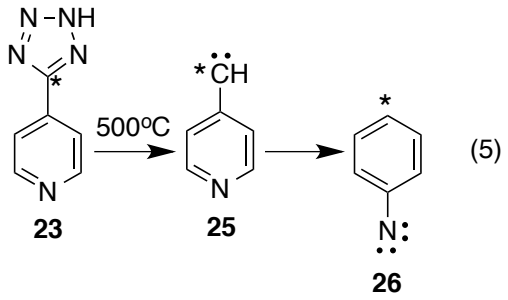
Scheme 8. The new pathways of ring contraction of 2-pyridylcarbene **13**. * = ^{13}C.

3. 4-Pyridylcarbene. Mild FVT of 4-(5-^{13}C-5-tetrazolyl)pyridine **23** (90 atom-% ^{13}C) at 400 ^{o}C/10^{-3} mbar with deposition of the thermolysate with Ar at 22 K allowed the IR-spectroscopic observation of the 4-diazomethylpyridine **24** (^{13}C=N=N stretch 2091 cm^{-1}). The corresponding unlabeled compound absorbs at 2097 cm^{-1} (Eq. 4). Analogous deposition of **23**/**24** in a cryostat for ESR spectroscopy followed by photolysis at $\lambda > 365$ nm generated 4-pyridyl-(^{13}C-carbene) **25** (D/hc = 0.5301 cm^{-1}; E/hc = 0.0246 cm^{-1}; Eq. 4 and Figure S7, Supporting Information).[20] The ^{13}C label gave rise to hyperfine splittings of 44 G (Z_1), 96 G (X_2) and 86 G (Y_2). This allows a calculation[21] of the HCC angle in 4-pyridylcarbene **25** as 149.7^{o}, very close to the HCC angle in phenylcarbene (149.2^{o}).[21b]

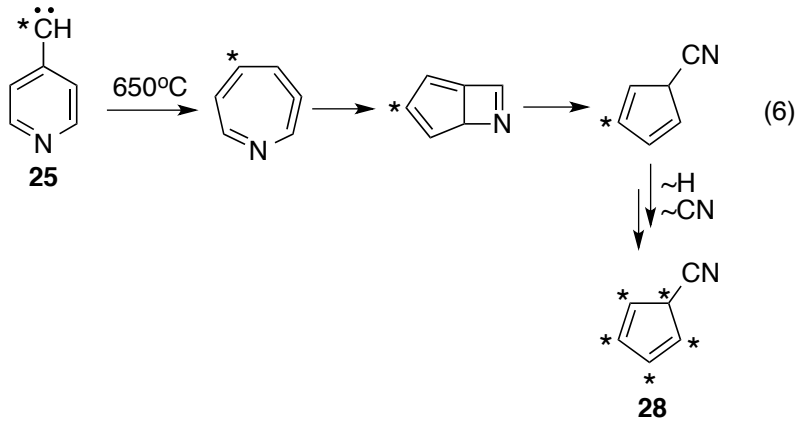


(4)

FVT of **23** at 500 ^{o}C with deposition of the product with Ar at 15 K in a cryostat for ESR spectroscopy gave rise to a strong XY_2 transition of phenylnitrene **26** (D/hc = 0.990 cm^{-1}, E/hc = 0.000 cm^{-1}; Eq. 5 and Figure S6, Supporting Information). Since a hyperfine coupling with the ^{13}C nucleus was not observable, the ESR spectrum does not identify the position of the label. The spectrum was identical with that of phenylnitrene **2T** obtained by FVT of phenyl azides **1** or **29** at 500 ^{o}C (Figures S5 and S6, Supporting Information).



Cyanocyclopentadiene **28** obtained by FVT of **23** at 650 ^{o}C/10^{-3} mbar did not contain any ^{13}C label on the CN group as demonstrated by ^{13}C NMR (Figure S3c, absence of enhancement of CN resonance at 117 ppm) as well as IR spectroscopy (absence of an isotopic shift of the CN vibration at 2224 cm^{-1}). The absence of ^{13}C label on CN is in accord with the new ring contraction mechanism (Eq. 6). It is also in accord with rearrangement of the carbene to phenylnitrene and direct ring contraction in phenylnitrene according to Scheme 9 described below.



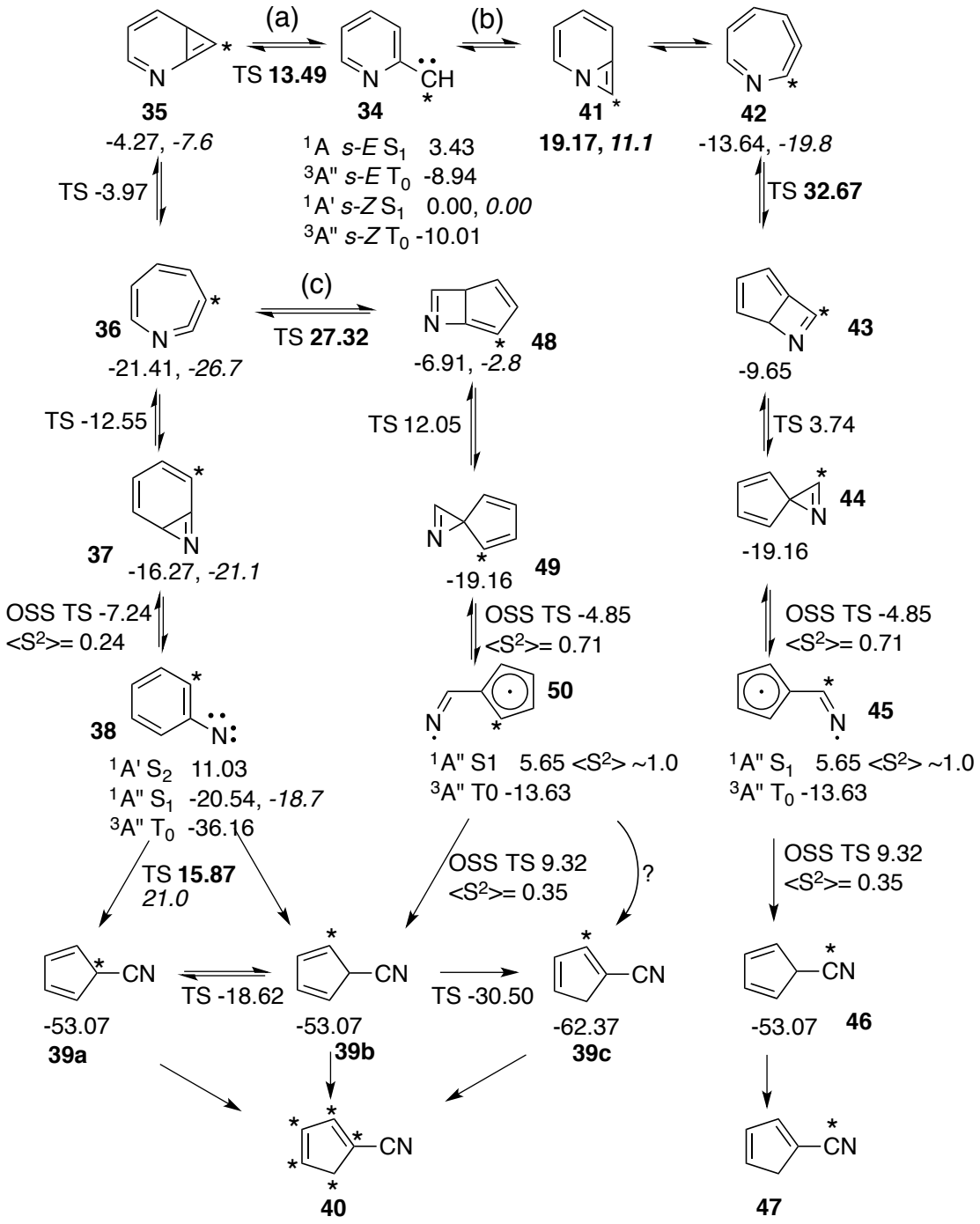
4. Phenylnitrene – 2-Pyridylcarbene. Reaction Mechanism. The new reaction mechanism (Scheme 8) has been corroborated computationally (Scheme 9). Most energies were calculated at the B3YP/631G* level of theory, which has been used frequently in studies of carbene and nitrene chemistry and shown to afford reasonable agreement with higher-level calculations.[9,10c,22] Here, the energies of open-shell singlet nitrenes and biradicals were estimated using the Ziegler-

Cramer method.[23] The species **45** and **50** are open-shell singlet biradicals rather than carbenes. They have triplet ground states. They are the links between the azaspiro[4.2]heptatrienes **44** and **49** and the cyanocyclopentadienes **39b** and **46**. They are formed with modest activation energies, but the spin expectation values $<S^2>$ of ~1 indicate significant spin contamination. The energy of the open-shell singlet nitrene **38** and the transition state for its ring contraction to cpCN **39a**/**39b** were also calculated at the CASPT2/cc-p-VDZ//CASSCF(8,8)/cc-pVDZ level (Scheme 9), and the structures of the transition states **38-39**, **34-41**, **41-42**, and **34-35** were also calculated at the CASSCF/6-31G* level (Figure 1). The energies of **2**, **3**, **4** and **6** (corresponding to **38**, **37**, **36** and **34** in Scheme 9) have been calculated previously by Karney and Borden at several levels of theory, including CASSCF(8,8)/6-31G* and CASPT2N/6-31G*.[24]

The activation barrier for the concerted ring contraction in open-shell singlet phenylnitrene $\mathbf{38S_1}$ is 31 kcal/mol at the CASPT2 and 26 kcal/mol at the B3LYP/6-31G* level (Scheme 9). The transition state for this reaction (^{1}Ph-N to CpCN), **TS38-39**, is shown in Figure 1 at the CASSCF level and in Figure S8 at the B3LYP level. This transition state is formally related to the "prefulvene" biradical invoked in benzene photo-isomerization by Bryce-Smith and Longuet-Higgins.[25a] We have not been able to locate an intermediate with the structure of **TS38-39**. The concerted ring contraction reaction might be considered to be coarctate in the terminology of Herges.[25b]

2-Pyridylcarbene **34** faces two activation barrier for cyclization/ring expansion according to routes a and b of 13 and 19 kcal/mol to yield **35** and **42**, respectively. Although **41** is formally antiaromatic, the barrier of route b is only ca. 5 kcal/mol higher than that for route a. The structures of **41** and **TS34-35** are depicted in Figure 1 and in Figure S8. Interestingly, **41** is a transition stste at the B3LYP level, but it is an intermediate at the CASSCF level. One can

understand the cyclization of 2-pyridylcarbene **34** to azirine **41** in terms of an interaction between the nitrogen lone pair and the vacant p orbital on the singlet carbene. The subsequent ring expansion **41** → **42** is highly exothermic (31-34 kcal/mol). The highest activation barrier in Scheme 9 is the one for the transannular ring closure in the cyclic allene **42** to the azabicyclo[3.2.0]heptatriene **43** (ca. 33 kcal/mol relative to the singlet carbene **34**). However, such barriers are readily overcome under the conditions of FVT. CpCN **39c**/**40**/**47** is a thermal sink and thus the end product of both reaction paths.



Scheme 9. Calculated energies in kcal/mol relative to *s-Z*-2-pyridylcarbene **34S$_1$** (-286.158765 Hartree). TS values in bold are for the purpose of comparison. Values in normal font are at the B3LYP/6-31G* + ZPVE level. Values in *italics* are at the *CASPT2/cc-p-VDZ//CASSCF(8,8)/cc-pVDZ* level for **38** and **TS38-39**, and at the *CASPT2/ANO-L//CASSCF(8,8)/ANO-L* C,N[4s3p1d]/H[2s1p] level for other structures. * = ^{13}C label.

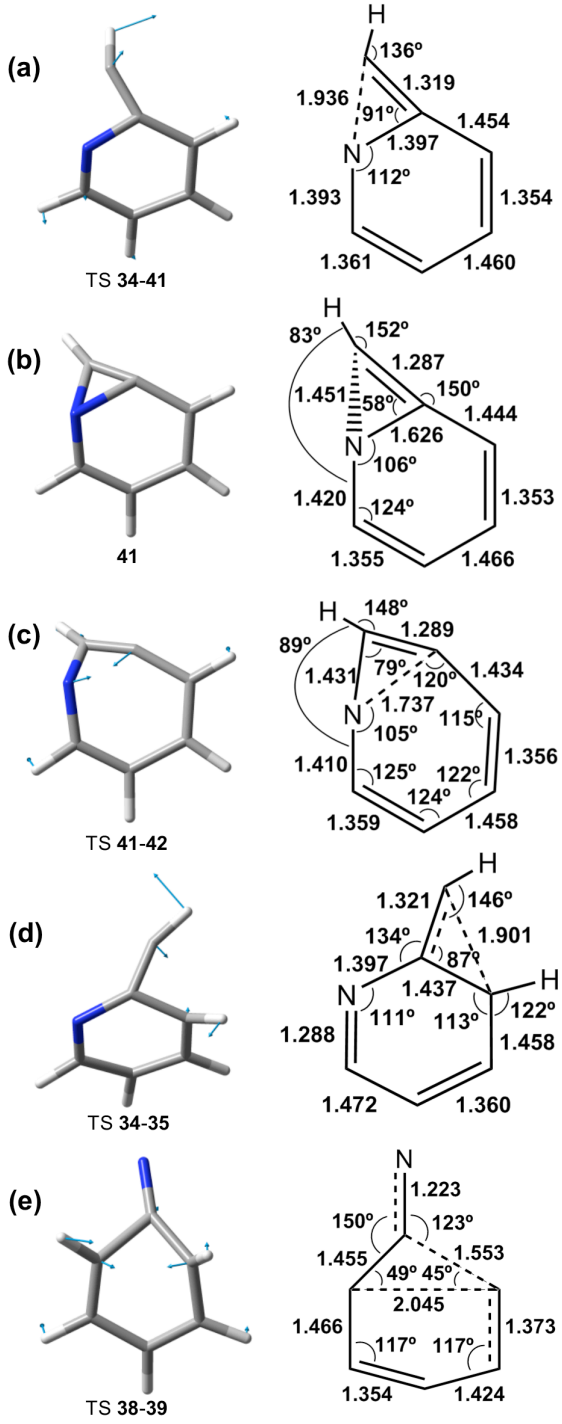
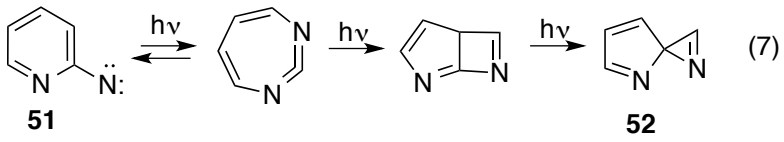


Figure 1. Structures of (a) **TS34-41** (2-pyridylcarbene ring closure to N1), (b) azirine **41**, (c) **TS41-42** (ring expansion of **41**), (d) **TS34-35** (2-pyridylcarbene ring closure to C3), (e) **TS38-39** (phenylnitrene-cyanocyclopentadiene) with displacement vectors, bond lengths (Å) and bond

angles at the CASSCF(8,8)/6-31G* level. Structures at the B3LYP/6-31G* level are shown in the Supporting Information, Figure S8.

The potential transannular cyclization of the cyclic ketenimine **36** to **48** will lead to the same labeling outcome as the direct nitrene route via **38S$_1$** (route c, Scheme 9). Further potential reaction paths are discussed in the Supporting Information. The postulated spiroazirines **44** and **49** (Scheme 9) are highly relevant: in the case of matrix photolysis of 2-pyridylnitrene **51** the corresponding spiroazirine **52** is directly observable[26] (Eq. 7). Further details are given in the Supporting Information, Scheme S1.



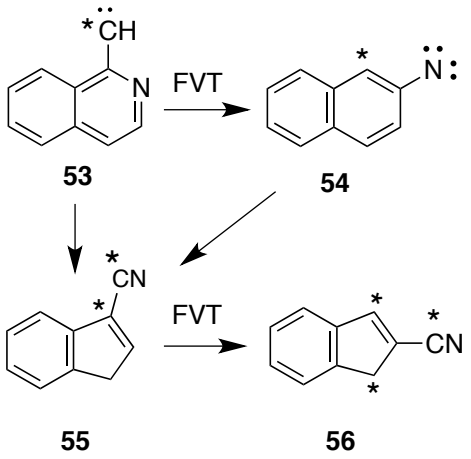
(7)

The spiroazirines are lower in energy than the neighboring azabicyclo[3.2.0]heptatrienes **43** and **48** and the biradicals **45** and **50**, but due to the low barriers between them, all these species are likely to be involved in the FVT reactions.

Because singlet phenyl nitrene **38S$_1$** (Scheme 9) is significantly more stable (lower in energy) than 2-pyridylcarbene **34S$_1$**,[1d,27] the nitrene route a is downhill all the way from the carbene to cpCN **40**. Experimentally, a 3:1 ratio of the nitrene to carbene routes was established[14] (Scheme 3), i.e. there is a preference for the nitrene route a. It must be kept in mind that reactions under the FVT conditions employed here are not amenable to treatment by the usual Arrhenius equation. The activation barrier of only 26-31 kcal/mol for ring contraction in singlet phenylnitrene **38S$_1$** would suggest that this reaction takes place very easily. However, this is not the case. As mentioned above, phenyl azide forms azobenzene and aniline very easily on FVT, but the formation of cpCN requires violent, virtually explosive conditions. It is only under

these conditions that appreciable yields of cpCN are obtained. The probable reason is that the ground state of phenylnitrene is the triplet **38T$_0$**, the rate of intersystem crossing (ISC) from the singlet **38S$_1$** is of the order of 10^6 s^{-1} in solution at RT,[2] and once the triplet has formed, azobenzene and aniline will be by far the major products. Therefore, only those nitrenes **38S$_1$** that have excess energy will be able to compete effectively with ISC and lead to cpCN. We have reported another case, of trifluoromethylphenylcarbenes, where rearrangement on the singlet energy surface competes with ISC to the triplet carbenes.[28] It is always much easier to obtain cyanocyclopentadienes from tetrazolylpyridines such as **12** and **23**; milder reaction conditions are required, and the yields are better. A logical reason for this is that the pyridylcarbenes already enter the energy surface with significant excess energy[1d,e] and, as shown in Scheme 9, a portion of the cpCN product (**47**) is formed via the non-nitrene route b and possibly also route c. Furthermore, the S-T splitting in carbenes is much smaller; therefore, the hetarylcarbens may react in the singlet state even when the ground state is a triplet.[7d]

The labeling patterns in the cyanoindenes **55** and **56** obtained by rearrangement of 1-isoquinolylcarbene **53** via 2-naphthylnitrene **54** (Scheme 10)[14] are explained in analogy with the phenylnitrene–2-pyridylcarbene mechanism shown in Scheme 9. This will be the subject of a separate publication.

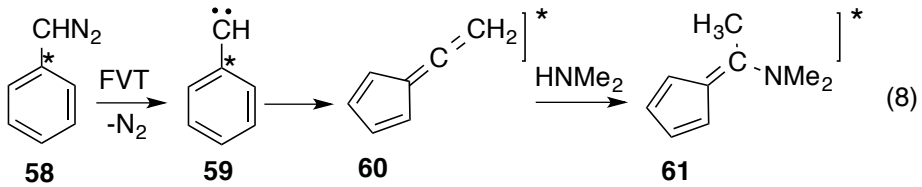


53 **54** **55** **56**

Scheme 10. Products of rearrangement of 1-isoquinolyl-^{13}C-carbene via 1-^{13}C-naphthylnitrene.

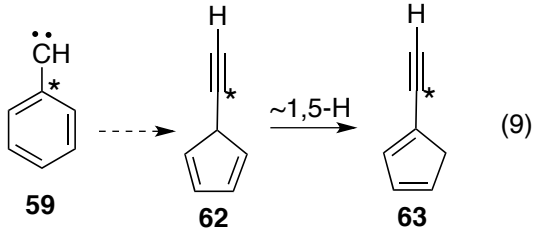
5. Phenylcarbene. The new mechanism of ring contraction in the hetarylcarbenes (routes b and c in Schemes 8 and 9) shares essential features with the mechanisms of rearrangement of 2-pyridylnitrene to cyanopyrroles[26] and of phenylcarbene **59** to fulvenallene **60** (Scheme 11),[19,29,30] and allow a unified description of all these reactions. The phenylcarbene rearrangement[28,29,31] and the mechanism of formation and thermal reactivity of fulvenallene have received much attention recently,[32] especially because fulvenallene is formed in combustion processes by dehydrogenation of the benzyl radical,[33] and it may also be formed in interstellar or planetary environments.[32c]

Fulvenallene **60** was generated by FVT of 1-^{13}C-phenyldiazomethane (60 atom-% ^{13}C) **58**, itself generated by thermolysis of the sodium salt of benzaldehyde tosylhydrazone **57**, and assayed by ^{13}C NMR spectroscopy of the 6-dimethylamino-6-methylfulvene derivative **61** formed by addition of dimethylamine (Eq. 8).[19,34]



58 **59** **60** **61** (8)

Under the mildest possible conditions where fulvenallene **60** can be obtained (590 ^{o}C/5-7 mbar N_2 as carrier gas, which serves to collisionally deactivate the primary product, thereby disfavoring further rearrangement) **60** was obtained with a large excess of ^{13}C label on the quaternary carbon atom C5 (Scheme 11 and Figure S9, Supporting Information).[19] This clearly demonstrates that, in contrast to the case of phenylnitrene described above, a simple ring contraction, for example to ethynylcyclopentadiene **63** (Eq. 9), was not occurring, or if it was, it would account for only a very minor fraction of the product, since the C6 carbon in **60** is one of the last to become labeled (cf. Scheme 11).

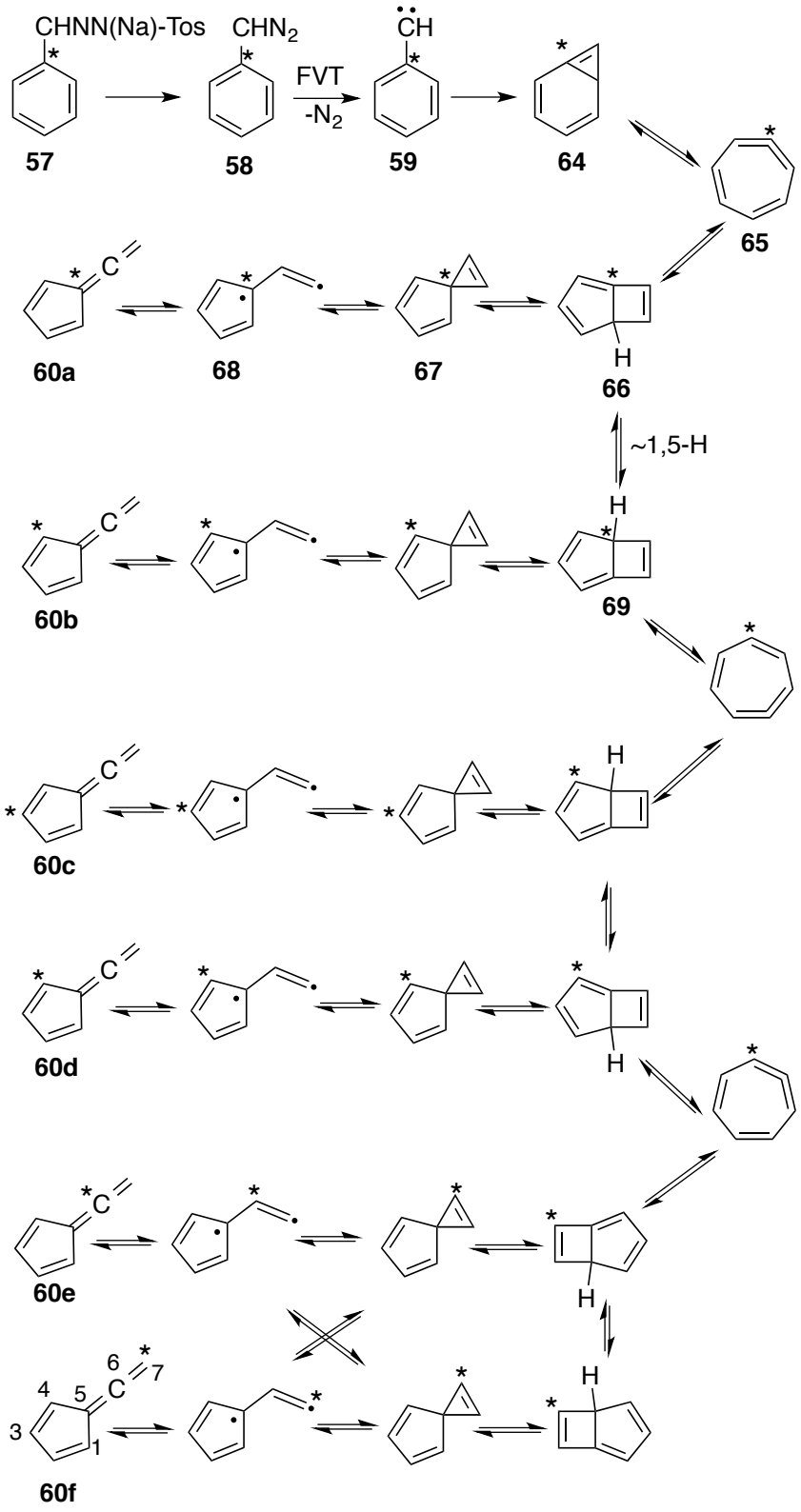


(9)

1-Ethynylcyclopentadiene **63** is in fact formed, usually as a minor constituent relative to fulvenallene **60** and increasing at higher temperatures,[35,36a] but the labeling experiment shows that it cannot be a principal product of direct rearrangement of phenylcarbene **59**. Its mechanism of formation is described below in the context of Scheme 12.

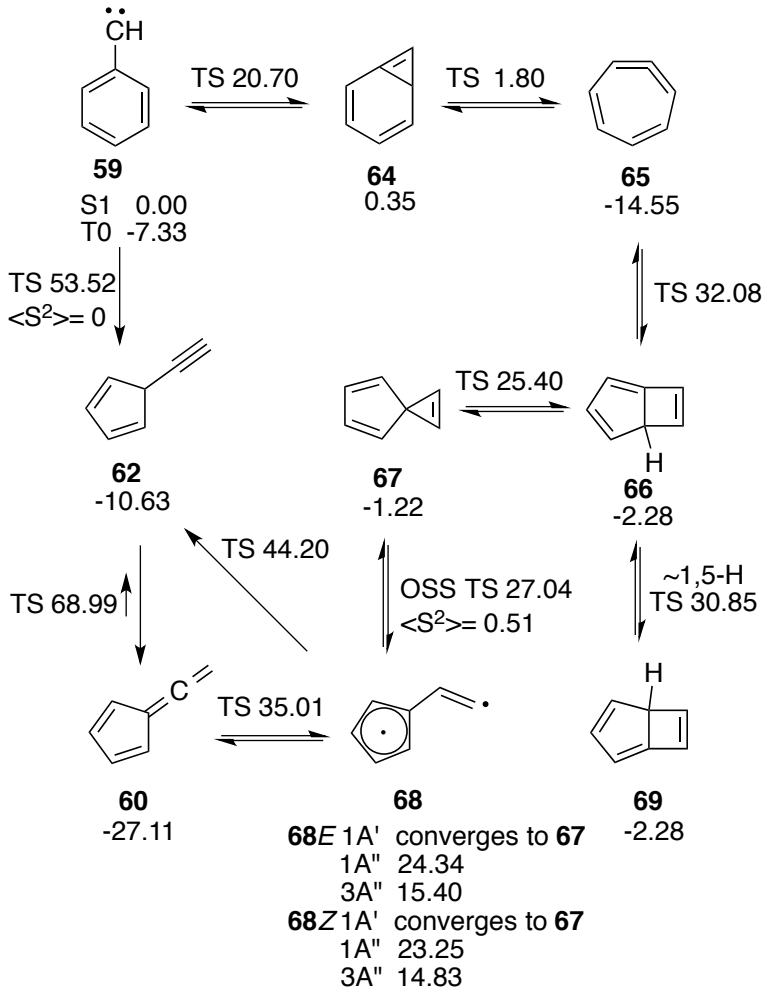
Even under these mildest FVT conditions, all carbon atoms in **60** were labeled, in the order C5 >> C1(C4) > C2(C3) > C6 > C7.[19] Increasing the FVT temperature to 700 ^{o}C/10^{-3} mbar resulted in almost complete carbon scrambling with only a small excess at C5, and at 900 ^{o}C/10^{-3} mbar uniform carbon scrambling was achieved (Figure S8).[19] The mechanism shown in Scheme 11 explains the results. The key step is the transannular cyclization of cycloheptatetraene **65** to bicyclo[3.2.0]hepta1,3,6-triene **66**. A 1,5-C shift in **66** can generate the spirocyclopropene **67** and then the biradical/vinylcarbene **68**, which leads to the required fulvenallene **60a**. A 1,5-H shift in

66 converts it to **69**, which now results in labeling at C1 in fulvenallene **60b**. Continuation of this process eventually leads to complete carbon randomization (Scheme 11), and the sequence of rearrangements required for this reflects the observed order of labeling at the various positions.



Scheme 11. The phenylcarbene – fulvenallene rearrangement. * = ^{13}C label (60 atom-% in **57**).

Calculations of most of the reaction paths in Scheme 11 at the G2(MP2,SVP) and B-LYP/6-311+G(3df,2p)+ZPVE levels were reported previously.[29] Further calculations concerning the 1,5-H shifts were reported by Patterson and McMahon,[30c] who found that the activation barriers for the two key steps, **65** → **66** and **66** → **69** were almost identical. We have now carried out further calculations of the whole energy surface at the B3LYP/6-31G*+ZPVE level and report the relevant data in Scheme 12.

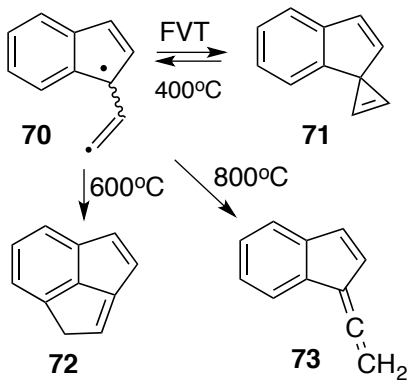


Scheme 12. Calculated energies at the B3LYP/6-31G* + ZPVE level relative to phenylcarbene S_1 (-270.115340 Hartree). Energies of open-shell singlet (OSS) biradical **68** have been corrected by using the Ziegler-Cramer method.[23]

It is seen in Scheme 12 that there is a relatively low-energy but indirect path from phenylcarbene to fulvenallene, **59** → **64** → **65** → **66** → **67** → **68** → **60**. None of the barriers are higher than 35 kcal/mol relative to phenylcarbene. The biradical species **68** is an open-shell singlet (OSS), which is easily understood in terms of delocalization of one p electron in the cyclopentadiene ring, while the remaining electron stays in a σ-type orbital on C7. We have considered the involvement of this biradical since our earliest investigations in this area,[19] but it has been missed in previous computational studies, which only considered closed-shell species.[29,32] The higher-lying closed-shell singlet of **68** has more carbene character (fulvenyl-6-carbene) but is not a minimum,[32] as it converges to the spiro-compound **67**. The transition state for ring closure of the OSS **68** to spiro-compound **67** lies only a few kcal/mol above **68**, although there is modest spin contamination ($<S^2> \sim 0.5$). The direct ring contraction **59** → **62** has a much higher activation barrier (53.5 kcal/mol relative to phenylcarbene) and is not competitive in agreement with the labeling results, which exclude the direct formation of **62** (Eq. 9). Instead, 5-ethynylcyclopentadiene **62** can form from the biradical **68** with a barrier of 44 kcal/mol. The more stable, conjugated 1-ethynylcyclopentadiene **63** can then form by a straightforward 1,5-H shift (Eq. 9). Because all the steps in Scheme 15 are reversible, the ethyne **63** could also in principle form by reversion of the whole reaction sequence (**60** → **66** → **65** → **59** → **62** → **63**),[32a] but this would again involve the 53.5 kcal/mol barrier. Furthermore, although the calculated barrier for a direct 1,4-H shift converting fulvenallene **60** to ethynylcyclopentadiene **62** is high (86 kcal/mol above **60**, it must be kept in mind that FVT is not a wall-less method, and hydrogen shifts in particular can be catalyzed by wall-collissions;[16] therefore the formation of **63** as a secondary product of H-migration in fulvenallene **60** is a very likely process. Note also that,

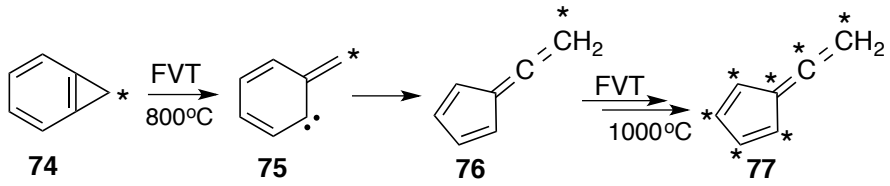
in all our work on hetarylnitrenes and hetarylcarbenes, we have never seen the formation of ethynylazoles.

It is worth mentioning that strong evidence for the validity of the reaction mechanism put forward in Schemes 11 and 12 was obtained in the corresponding benzo series, where rearrangement of carbene or biradical **70** (formed by FVT of benzofulvenyl-8-diazomethane) afforded the isolable compounds **71**, **72**, and **73** (Scheme 13).[30a]



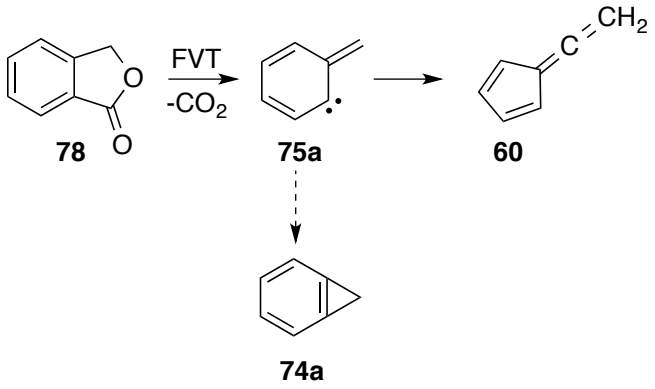
Scheme 13. Isolable rearrangement products arising from FVT of benzofulvenyl-8-diazomethane.

The scrambling mechanism shown in Scheme 11 implies that the whole rearrangement sequence from phenylcarbene to fulvenallene is reversible under high-temperature FVT conditions. Consequently, fulvenallene itself must undergo carbon scrambling at sufficiently high temperatures. Indeed, this was demonstrated to be the case by FVT of 1-^{12}C-benzocyclopropene (i.e. ^{13}C-depleted) **74**.[19] At 800 ^{o}C the majority of the label stayed at the C7 position in fulvenallene **76** in agreement with simple Wolff-rearrangement of **75**. However, at 1000 ^{o}C, ca. 80% of the label was scrambled over all carbon atoms, and repyrolysis at 1050 ^{o}C of the fulvenallene isolated from a pyrolysis of **74** at 750 ^{o}C resulted in ~100% label scrambling over all carbon atoms[19] (**77**, Scheme 14).



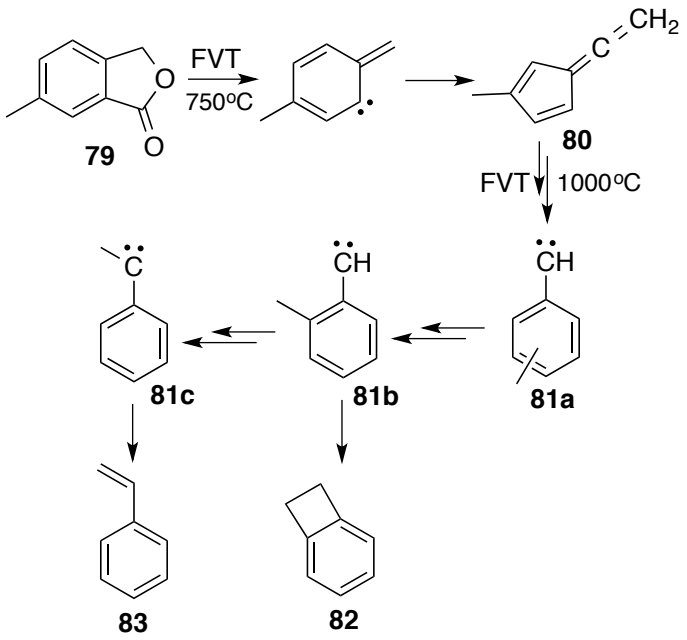
Scheme 14. FVT of benzocyclopropene. * = ^{12}C (^{13}C-depleted).

The pyrolysis of phthalide **78** is a convenient method of synthesizing fulvenallene.[36] The same intermediate **75a** as in the benzocyclopropene pyrolysis is assumed to be involved (Scheme 15). Incidentally, the "awful olefinic smell" ascribed to fulvenallene by Wiersum[36b] is not due to fulvenallene but to traces of benzocyclopropene **74a** formed by cyclization of **75a**.



Scheme 15. Synthesis of fulvenallene from phthalide.

Furthermore, the reversibility demands that a methylfulvenallene **80** can revert to a tolylcarbene **81** and hence undergo the tolylcarbene rearrangement[37] (**81a** ⇄ **81b** ⇄ **81c**) to benzocyclobutene **82** and styrene **83**. This too was confirmed by FVT of 6-methylphthalide **79** (Scheme 16).[19]



Scheme 16. Reversion of methylfulvenallene into the tolylcarbene rearrangement.

We conclude therefore that the rearrangement mechanism shown in Schemes 11 and 12 completely satisfies all available experimental observations.

Conclusion

The cyanocyclopentadiene (cpCN) **32** formed by high-temperature FVT of 1-^{13}C-phenyl azide **29** is labeled exclusively on the CN carbon, and the aniline **31** also formed is labeled exclusively at C1 (Scheme 7). These results establish a *direct ring contraction in phenylnitrene* and rule out the operation of the cycloperambulation mechanism and the occurrence of 1,3-H shifts in 2-azabicyclo[4.1.0]hepta-2,4,7-triene intermediates (Scheme 2). However, the cpCN obtained by rearrangement of 2-pyridyl-(^{13}C-carbene) **34** carries ^{13}C label on all carbon atoms, thereby revealing a ring contraction mechanism *different from that of phenyl azide*. A new mechanism is put forward, whereby a major portion of 2-pyridylcarbene rearranges via 1-azacyclohepta-1,2,4,6-tetraene **36** to phenylnitrene, which then undergoes direct ring contraction to cpCN.

Another portion of 2-pyridylcarbene undergoes ring expansion to 4-aza-cyclohepta-1,2,4,6-tetraene **42**, which then by trans-annular cyclization affords 6-azabicyclo[3.2.0]cyclohepta-1,3,5-triene **43**. Further rearrangement of **43** via the spirotriene **44** and biradical/vinylnitrene **45** affords cpCN with the label on the CN group (Schemes 8 and 9). The same type of mechanism also accounts for the labeling patterns in 3- and 2-cyanoindenes **55** and **56** obtained from 1-isoquinolyl-(^{13}C-carbene) **53** (Scheme 10). The ring expansion/transannular cyclization and ring opening mechanism also describes the labeling pattern in fulvenallene **60** formed from phenylcarbene **59** by FVT of 1-^{13}C-phenyldiazomethane **58** (Schemes 11 and 12). The mechanistic pathways are supported by calculations at the B3LYP/6-31G* and in part CASPT2//CASSCF(8,8) levels.

Computational Method

Standard DFT calculations were performed using the Gaussian 03 suite of programs.[38] Geometry optimizations and frequency calculations were computed at the B3LYP/6-31G* level, whereby the energies of the open-shell singlet nitrenes (S_1, ^{1}A") was estimated using the Ziegler-Cramer method.[23] Energies of the phenylnitrene **39** and the transition state for rerrangement to cycnocyclopentadiene **39** were also calculated at the CASPT2/cc-pVDZ//CASSCF(8,8)/cc-pVDZ levels of theory. Structures of other species in Figure 1 and Scheme 9 were calculated at the CASSCF(8,8)/B3LYP/6-31G* level, and energies at the CASPT2/ANO-L//CASSCF/ANO-L level using MOLCAS (the full description of the ANO-L basis set is ANO-L C,N[4s3p1d]/H[2s1p].[39] Zero point vibrational energy corrections have been applied in all calculations.

Experimental Section

General. Apparatus for FVT,[16] matrix isolation and ESR spectroscopy,[16,40] and pulsed pyrolysis[16,41] were as described.

1-^{13}C-Phenyl azide. Benzoic acid-1-^{13}C (90 atom-% ^{13}C; 1 g, 8.13 mmol) was dissolved in 15 mL of $CHCl_3$, and 9 mL of H2SO4 (98 %) was added. The solution was warmed to 40 ^{o}C on a water bath, and 1g (15.4 mmol) of finely powdered NaN_3 was added slowly. The resulting mixture was stirred at 40 ^{o}C for 20 h. After cooling to RT, 60 mL of water was added to the mixture, which was then alkalinized with KOH. The liquid supernatant was decanted, and the residue was washed with ether. The supernatant was extracted 3 times with ether, and the ether extracts and washing were combined and dried over Na_2SO_4. The solvents were removed by distillation, and the last traces were removed briefly in high vacuum to yield 501 mg of 1-^{13}C-aniline (5.3 mmol; 65 %). This material was dissolved in a warm mixture of 1 mL of H_2SO_4 and 6 mL water, which was then cooled to 0 ^{o}C. $NaNO_2$ (0.44 g, 6.4 mmol) dissolved in 4 mL of ice-cold water was added with stirring at 0 ^{o}C in the course of 1 h. An ice-cold solution of NaN_3 (0.58 g, 9.0 mmol) in 4 mL of water was added at 0 ^{o}C with stirring. The mixture was stirred for another hour at 0 ^{o}C and then overnight at RT. The resulting mixture was extracted three times with hexane, the extract was dried over Na_2SO_4 and filtered, and the sodium sulfate was re-extracted with hexane. Hexane was distilled from the combined solutions, and the resulting phenyl azide was purified by chromatography on silica gel, eluting with hexane. After distillation of the hexane, 375 mg (3.13 mmol; 38 % based on benzoic acid) of 1-^{13}C-phenyl azide was obtained. IR (Ar matrix, 12 K) 2130s, 2100w, 2084w, 1595m, 1490m, 1294m, 1269m, 1117w, 1076w cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 140.1 (90 % ^{13}C, rel. intensity 100; C1), 129.8 (8; C4), 124.9 (3; C4), 119.1 (0.5; C2); ^{13}C-^{13}C coupling constants: δ 119.1 (*ortho*-C, 65.2 Hz), δ 124.9 (*para*-

C, 10.1 Hz).[42] The unlabeled phenyl azide had IR (Ar matrix, 12 K) 2136s, 2102w, 2089w, 1600m, 1497m, 1299m, 1275m, 1132w, 1116w, 1078w cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 140.1 (C1), 129.8 (CH), 124.9 (CH), 119.1 (CH).

FVT of 1-^{13}C-Phenyl azide. (a) FVT of 1-^{13}C-phenyl azide at 500 $^oC/10^{-4}$ mbar with isolation of the product with Ar on a Cu rod at 15 K in a cryostat for ESR spectroscopy gave rise to an ESR spectrum of the labeled phenylnitrene, XY_2 = 6981.1 G; D/hc = 0.990 cm^{-1}, E/hc = 0.000 cm^{-1}; microwave frequency 9.77 GHz (Figure S5, Supporting Information), which was indistinguishable from that of the unlabeled phenylnitrene[8] (i.e. no hyperfine ^{13}C coupling was observed).

(b) 1-^{13}C-phenyl azide (300 mg) was subjected to preparative FVT at 800 ^oC with an initial vacuum of 10^{-3} mbar provided by a two-stage oil diffusion pump, which was continuously pumping throughout the experiment. The system was rapidly evacuated with the liquid azide at RT. The azide was then rapidly warmed to 40-45 ^oC, and the sample flask was gently shaken to aid rapid evaporation of the azide. The resulting high concentration of azide at the entrance of the 800 ^oC pyrolysis tube sets up a shock wave, which heats the remaining liquid azide to over 100 ^oC, and all the azide evaporates in a matter of seconds. The products were isolated in liq. N_2 cold traps and consisted largely of 1-cyanocyclopentadiene (yield up to 18 % in unlabeled runs)[1d] and aniline among other compounds.[1c] Pyrolysis at milder conditions, e.g. 500 $^oC/10^{-1}$ mbar affords only azobenzene and aniline (e.g. 300 ^oC/0.05 mbar: 0.5 % aniline, 82 % azobenzene; 500 ^oC/0.1 mbar: 40 % azobenzene in unlabeled runs).[1d] After the end of the experiment, the content of the cold traps was taken up in $CDCl_3$ and analyzed by ^{13}C NMR spectroscopy. Cyanocyclopentadiene is purified by rapid vacuum distillation and gas chromatography and

should be stored at or below -20 °C to avoid dimerization. However, the dimer which forms at RT can be de-dimerized by fractional distillation through a short Vigreux column or by gas chromatography.

Data for unlabeled aniline: ^{13}C NMR ($CDCl_3$) δ 115.2 (*ortho*-C), 118.6 (*para*-C), 129.3 (*meta*-C), 146.5 (C1). The aniline from the labeled FVT was labeled exclusively on C1 (146.5 ppm). The natural abundance *ortho* and *para* carbons showed ^{13}C-^{13}C couplings of 61.8 and 9.4 Hz, respectively.[41]

Data for unlabeled cyanocyclopentadiene: ^{13}C NMR ($CDCl_3$) δ 44.3 (C5), 113.1 (C1) 116.8 (CN), 132.3 (C2), 139.2 (C3), 147.1 (C4). The carbon resonances were assigned by measurement of the ^{13}C-^{13}C coupling constants for the labeled sample described here and the ^{13}C-H coupling constants described under FVT of **23** below.

The cyanocyclopentadiene obtained by FVT of 1-^{13}C-phenyl azide was exclusively labeled on the nitrile carbon. No label in excess of natural abundance was detectable at the other C atoms. ^{13}C-^{13}C coupling constants: δ 44.3 (5.3 Hz), 132.3 (7.4 Hz), 139.2 (3.4 Hz), 147.1 (2.7 Hz).

4-(5-^{13}C-5-Tetrazolyl)pyridine 23. Butyl lithium (2.43 g, 38 mmol (19 mL of a 2 M solution in hexane)) was added dropwise to 4-bromopyridine in 180 mL of anhydrous ether at -70 °C in a system attached to a vacuum line. The system was evacuated and degassed and then cooled to ca. 77 K in liq. N_2. In a separate flask, $Ba^{13}CO_3$ (90.4 atom-% ^{13}C; 5 g; 25.3 mmol) was treated with 100 mL of H_2SO_4 while stirring magnetically and heating at 60 °C. The ^{13}C-labeled CO_2 so formed was condensed through a $CaCl_2$ drying tube into the flask containing the organolithium solution, which was now warmed to -60 °C. This reaction mixture was stirred magnetically for 1 h and then allowed to warm to RT. It was frozen at 77 K again twice in order to condense any remaining CO_2. The resulting mixture was acidified with 30 mL 2.5 N HCl and then alkalinized

with NaOH to pH 12 and extracted with ether continuously for 12 h in order to remove organic material. The isonicotinic (4-pyridinecarboxylic) acid so formed was liberated by acidification to pH 2.7 and then extracted with ether continuously for 100 h, after which time the solvent was removed in vacuum and the product purified by vacuum sublimation. Yield 2.8 g (84 %); mp 300-303 ^{o}C (lit.[43] 310-304 ^{o}C (unlabeled)); MS *m/z* 124 (100), 123 (9.8). MS of the unlabeled material: *m/z* 124 (10), 123 (100).

A suspension of the isonicotinic acid in in 200 mL of THF was esterified by adding a solution of 1 g (23.8) mmol of diazomethane in ether at 0 ^{o}C. After warming to RT, the solution was filtered with active carbon and then evaporated to dryness to afford 2.1 g (95%) of methyl isonicotinate, mp 8 ^{o}C (lit.[44] 8 ^{o}C (unlabeled)); ^{1}H NMR δ 4.05 (d, 3 H, J_{CH} = 4 Hz), 7.8-8.1 (m, 2 H), 8.8-9.0 (m, 2 H). The ^{1}H NMR spectrum was identical with that of the unlabeled material except that the signal at δ 4.05 was a singlet in the unlabeled compound.

The labeled ester was converted to isonicotinic amide using the method of Meyer,[45] yielding 1.73 g (93 %), mp 152-154 ^{o}C (lit.[45] 152-154 ^{o}C (unlabeled)). This was further converted to the labeled pyridine-4-carbonitrile as reported by Meyer[45] to afford 646 mg (44%), mp 77-78 ^{o}C (lit.[45] 79 ^{o}C (unlabeled)).

A mixture of the labeled pyridine-4-carbonitrile, 450 mg (8.4 mmol) of NH_4Cl, and 550 mg(8.5 mmol) of NaN_3 in 30 mL of anhydrous DMF was heated at 95 ^{o}C under N_2 for 48 h. The resulting solution was evaporated to dryness, the solid was dissolved in hot water, and this solution was acidified with 2.5 N HCl to pH 2 and allowed to cool. The yellow precipitate was filtered and dried in vacuum over P_2O_5 to yield 755 mg (83 %) of the desired 4-(5-^{13}C-5-tetrazolylpyridine, mp 270 ^{o}C with decomposition (lit.[46] 268-269 ^{o}C (unlabeled)); MS *m/e* 149 (3), 148 (38), 147 (3). MS of the unlabeled compound: *m/e* 148 (4), 147 (40).

FVT of 4-(5-^{13}C-5-Tetrazolyl)pyridine 23. (a) A 10 mg sample was subjected to mild FVT at 400 ^{o}C/10^{-3} mbar with isolation of the product with Ar at 22 K to produce a matrix. 4-Diazomethylpyridine **24** was observed at 2091 cm^{-1} (C=N=N stretch). The corresponding unlabeled compound absorbs at 2097 cm^{-1}. When the Ar matrix was condensed on a Cu rod at 15 K for ESR spectroscopy and then photolysed at $\lambda > 365$ nm ($NiSO_4/CoSO_4$ filter), the ESR spectrum of 4-pyridyl-(carbene-^{13}C) was obtained (Figure S7, Supporting Information); *D/hc* = 0.5301 cm^{-1}; *E/hc* = 0.0246 cm^{-1}; The ^{13}C label gave rise to hyperfine splittings of 44 G (Z_1), 96 G (X_2) and 86 G (Y_2) from which a carbenic HCC angle of 149.7^{o} was calculated.[21]

(b) FVT of **23** at 500 ^{o}C/10^{-3} mbar with deposition of the product with Ar at 15 K in a cryostat for ESR spectroscopy gave rise to the strong XY_2 transition of phenylnitrene at 6857.6 G (no hyperfine splitting observable), *D*/*hc* = 0.990 cm^{-1}, *E*/*hc* = 0.000 cm^{-1}; microwave frequency 9.45649 GHz; H_0 = 3374.4 G (Figure S5c, Supporting Information). The ESR spectrum was identical with that of phenylnitrene obtained by FVT of phenyl azides **1**,[8] or of **30** at 500 ^{o}C, or of triazolopyridine **7T**[8] at 300-450 ^{o}C/10^{-3} mbar.

(c) Preparative FVT of **23**. A sample of 200 mg of **23** was subjected to FVT at 400 ^{o}C/10^{-3} mbar. The starting material was sublimed into the FVT tube at 190-210 ^{o}C, and the product was isolated in a liq N_2 trap. After the end of the experiment, the product was dissolved in $CDCl_3$ and analyzed by ^{13}C NMR spectroscopy.

Data for the ^{13}C labeled aniline: δ 118.4 (dt, $^{1}J_{CH}$ = 165 Hz; $^{3}J_{CH}$ = 8 Hz; *para*-C). The remaining carbons in aniline were not labeled. For the unlabeled aniline, see under phenyl azide above.

Data for cyanocyclopentadiene: δ 44.1 (tt, $^1J_{CH}$ = 130, J_{CH} = 8 Hz, C5), 113.3 (s, C1), 131.9 (dt, $^1J_{CH}$ = 170, J_{CH} = 5 Hz, CH), 139.4 (dm, $^1J_{CH}$ = 175, J_{CH} = 5 Hz, CH), 147.0 (dm, $^1J_{CH}$ = 175, J_{CH} = 5 Hz, CH). All ring carbon atoms carried uniform ^{13}C labeling, but there was no measurable label above the noise level on the nitrile carbon (δ 116.8) (Figure S3c, Supporting Information).

2-(5-^{13}C-5-Tetrazolyl)pyridine 12. This compound was prepared from 2-bromopyridine (5 g; 31.6 mmol) and $Ba^{13}CO_3$ (90.8 atom-% ^{13}C) in the same manner as described for **23** above. This yielded 270 mg of **12**, mp 217-219 °C (lit.[47] 217-219 °C (unlabeled)); MS *m/e* 149 (3), 148 (20), 147 (3). MS of the unlabeled material: *m/e* 148 (3); 147 (20).

FVT of 2-(5-^{13}C-5-Tetrazolyl)pyridine 12. (a) A sample of 50 mg of **12** was subjected to preparative FVT at 400 °C/1 mbar N_2 as carrier gas. The sample flask was held at 140 °C, and the products were isolated in a liq. N_2 trap. The thermolyzate was taken up in ether, and azobenzene was separated by thick layer chromatography on silica gel, eluting with $CHCl_3$/MeOH 99:1. The isolated azobenzene had mp 68 °C (lit. 68.5 °C). MS *m/e* 185 (16), 184 (100). 183 (30). ^{13}C NMR ($CDCl_3$) δ 122.8 (*ortho*-C). No other carbon atom was labeled (Figure S5, Supporting Information).[48] A yield of up to 40 % of azobenzene was obtained in unlabeled runs.[1d] In addition, triazolo[1,5-*a*]pyridine **7T** was obtained in yields of 3-15 % in unlabeled runs.[1d]

(b) The tetrazole was subjected to FVT at 600 °C/10^{-3} mbar with isolation of the products in a liq. N_2 trap. After the end of the experiment, the volatile components were transferred in vacuum to an NMR tube and analyzed by ^{13}C NMR spectroscopy.

Data for aniline: δ 114.7 (*ortho*-C). No other carbon atom was labeled (Figure S2, supporting Information).

Data for cyanocyclopentadiene: δ 44.1, 113.3, 117.1, 131.9, 139.4, 147.4. The labeling ratio ring(total for 5 carbons): CN was ca. 3:1. (Figure S1, Supporting Information). Yields of 40-70 % were obtained in unlabeled runs.[1d]

1-^{13}C-Phenyldiazomethane 58 and ^{13}C-Labeled Fulveanallene 60. 1-^{13}C-Benzoic acid (60 atom-% ^{13}C) was reduced to 1-^{13}C-benzyl alcohol with $LiAlH_4$ and then oxidized to 1-^{13}C-benzaldehyde with pyridinium chlorochromate by using standard procedures. The aldehyde was treated with tosylhydrazine in THF to obtain the tosylhydrazone, and the sodium salt **57** was obtained with NaH in THF according to the standard procedure used previously for the unlabeled compound.[38] The solid salt was heated to 90 ^{o}C in the sublimation flask of the FVT apparatus, and the resulting vapor was passed through the FVT tube at various temperatures. Phenyldiazomethane **58** was detectable at temperatures up to ca. 500 ^{o}C. Fulvenallene **60** was formed as a yellow oil in increasing yield at temperatures between 590 and 900 ^{o}C and isolated in liq.-N_2 cold traps. This product was taken up in ether and treated with dimethylamine at RT to yield the yellow 6-methyl-6-dimethylaminofulvene **61**, which was assayed by ^{13}C NMR spectroscopy[34] (Figure S10). The mildest conditions for fulvenallene formation with minimal carbon scrambling in the ^{13}C-labeled runs were 590 ^{o}C in a stream of N_2 as carrier gas at 5-7 mbar; this serves to collisionally deactivate the fulvenallene, thereby hindering further rearrangement. Further FVT reactions at 600-900 ^{o}C were carried out at 10^{-3} mbar and resulted in increasing degrees of carbon scrambling with increasing temperature (Figure S8, Supporting Information).

ASSOCIATED CONTENT

Supporting Information Available. ESR spectra of phenylnitrene from several precursors, 4-pyridylcarbene and 2-naphthylnitrene; ^{13}C NMR spectra of ^{13}C-labeled 1-cyanocyclopentadiene, azobenzene, aniline, and 6-dimethylamino-6-methylfulvene, and computational data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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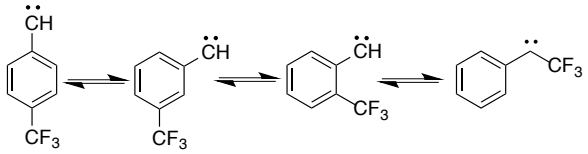

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