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[8] Cu_3 complexes analogous to **2a** and **2b** were obtained from 2-quinolyl-2,2′-[5,5′-bis(ethoxycarbonyl)]dipyrrolylmethane, and their X-ray structural analyses verified the structure of **2a**. Details will be reported elsewhere.

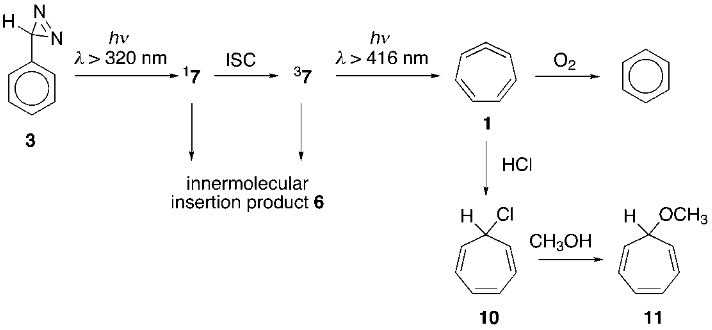
1,2,4,6-Cycloheptatetraene: Room-Temperature Stabilization inside a Hemicarcerand**

Ralf Warmuth* and Melissa A. Marvel

Dedicated to Professor Donald J. Cram
on the occasion of his 80th birthday

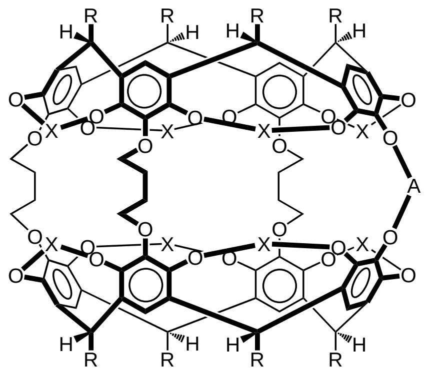
The phenylcarbene rearrangement is one of the most important and fascinating carbene rearrangements. Despite intense experimental and theoretical studies neither is the exact mechanism known nor have the energetics of the thermal interconversion between the involved intermediates been studied.[1, 2] Chapman and co-workers photochemically generated 1,2,4,6-cycloheptatetraene **1** at 15 K in argon and provided spectroscopic evidence for this highly strained allene.[3] Rapid dimerization at higher temperatures prevented a detailed study of the equilibration between **1** and cycloheptatrienylidene (**2**), which plays an important role in the solution-phase chemistry of both species.[4]

Incarceration in the inner phases of Cram's hemicarcerands is a novel, elegant, and extremely powerful way to stabilize reactive intermediates by preventing their dimerization.[5] This method has previously been used to stabilize cyclobutadiene and *o*-benzyne (1,2-didehydrobenzene) [6, 7] Here, we report the room-temperature stabilization of **1**, which we generated from phenyldiazirine (**3**) by a photochemical phenylcarbene rearrangement inside hemicarcerand **4** (Scheme 1).[8]



Scheme 1. Inner phase generation and chemistry of **1**. ISC = intersystem crossing.

We incarcerated **3** by reacting diol-host **5** with 1,4-butanediol dimethanesulfonate and Cs_2CO_3 in the presence of excess **3** in hexamethylphosphoramide.[9, 10] This reaction provided the hemicarceplex **4·3** in 80% yield (Figure 1a).[11] Photolysis ($\lambda > 320$ nm) of a degassed solution of **4·3** in $C_6D_5CD_3/CDCl_3$ (9:1) at 77 K gave the innermolecular phenylcarbene insertion product **6**. In the hope that a small isotope effect would slow down this competing reaction, we prepared $[D_{16}]$**4·3** in



4: X = CH_2; A = $(CH_2)_4$
$[D_{16}]$**4**: X = CD_2; A = $(CH_2)_4$
5: X = CH_2; A = H H
$[D_{16}]$**5**: X = CD_2; A = H H

R = $(CH_2)_4CH_3$

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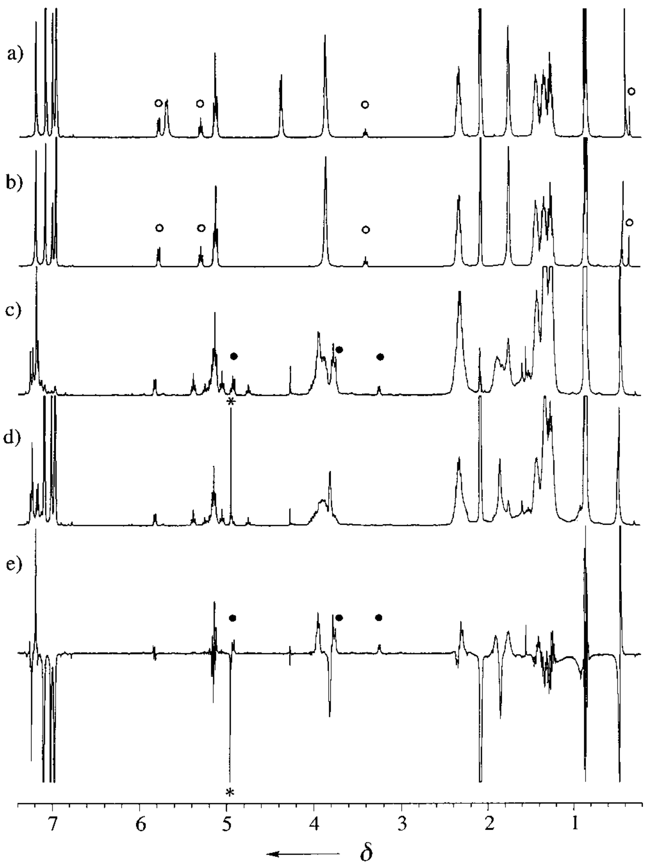
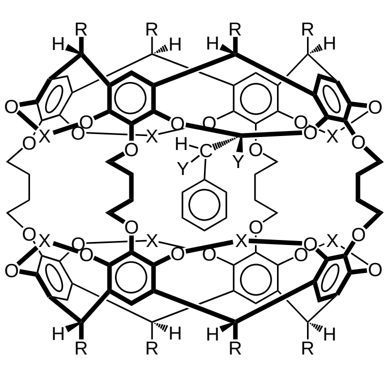
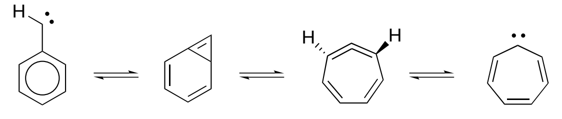


Figure 1. ^1H NMR spectra (400 MHz, [D$_8$]toluene, 20 °C) of **4 • 3** (a) and [D$_{16}$]**4 • 3** (b), as well as of a photolyzed solution of [D$_{16}$]**4 • 3** under oxygen free conditions (c) and after 1 hour of exposure to atmospheric oxygen (d). e) Difference spectrum between c) and d). Proton signals of [D$_{16}$]**4 • 1** point upwards, those of [D$_{16}$]**4** • benzene point downwards. Peaks marked with a circle, a black dot, and an asterisk indicate the ^1H nuclei of incarcerated **3**, **1**, and benzene, respectively.

which all eight acetal carbons are fully deuterated (Figure 1b). Indeed, after UV irradiation ($\lambda > 320$ nm at 77 K) of [D$_{16}$]**4 • 3** in [D$_8$]toluene, the room-temperature ^1H NMR spectrum of this solution revealed the formation of a new hemicarceplex in 12 % yield accompanied by mainly [D$_{16}$]**5**. Photolysis at 15.5 K improved the yield to 30 % (Figure 1 c). Addition of the triplet sensitizer [D$_8$]acetophenone to the bulk phase (15 % (v/v)) further increased the yield (60 %) and reduced the amount of [D$_{16}$]**6** (10 %) formed, consistent with the required excitation of triplet phenylcarbene ^{3}**7**.[3] The dramatic reduction in the amount of [D$_{16}$]**6** formed under sensitized conditions suggests that ^{1}**7** rather than ^{3}**7** undergoes the acetal C–H(D) insertion.



6 X = CH$_2$; Y = H
[D$_{16}$]**6** X = CD$_2$; Y = D
R = (CH$_2$)$_4$CH$_3$



7 **1** **2**

We assigned the newly formed hemicarceplexes to the cycloheptatetraene hemicarceplexes [D$_{16}$]**4 • 1** and **4 • 1** based on the spectroscopic properties and inner phase reactivity of the incarcerated guest. The FT-IR spectrum of [D$_{16}$]**4 • 1** in CDCl$_3$ shows a weak band at 1810 cm^{-1}, which is assigned to an allenic carbon–carbon stretching frequency of **1** which appeared at 1824 cm^{-1} and 1823 cm^{-1} in the argon-matrix isolation experiments.[2, 3] The three ^1H multiplets in the ^1H NMR spectrum of the incarcerated guest are highlighted in Figure 2. From homonuclear ^1H-^1H COSY and NOESY spectra, we conclusively assigned the multiplet at $\delta = 3.26$ to the protons H2 and H2′. The assignment of the remaining multiplets is based on the relative intensities of the cross peaks in the ^1H-^1H COSY and NOESY spectra. The cross peaks between the protons H1 and H2, and H1′ and H2′ are weaker than those between H2 and H3 and H2′ and H3′, respectively. Similar observations were made by Jones and Lu for the cycloheptatetraene platinum complex **8**.[12]

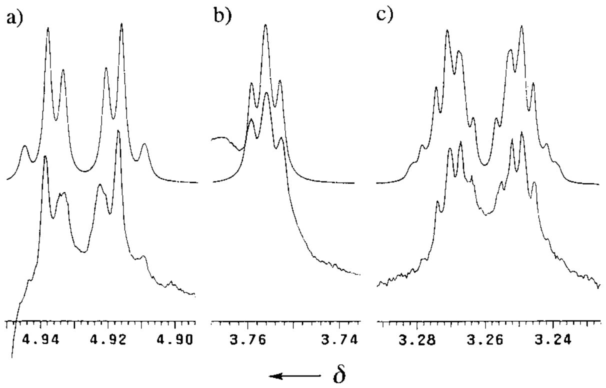
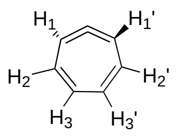
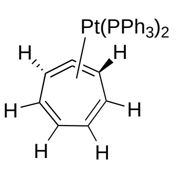


Figure 2. Part of a ^1H NMR spectrum (400 MHz, [D$_8$]toluene, 20 °C) of [D$_{16}$]**4 • 1**. The multiplets are given with the best fit (upper trace): a) H3/H3′; b) H1/H1′; c) H2/H2′.



1



8

We estimated the chemical shifts of the free guest as described earlier for *o*-benzyne using free cycloheptatriene **9** and hemicarceplex **4·9** as model compounds (Table 1).[7a] The predicted chemical shifts, the ^{1}H-^{1}H coupling constants (Table 2) obtained from a lineshape analysis,[13] and the sharpness of the resonances of the hemicarcerand's acetal protons in the ^{1}H NMR spectrum of **4·1** leave little doubt that **1** is the guest, rather than **2** for which matrix ESR studies suggest a triplet ground state.[14, 15]

Table 1. ^{1}H chemical shifts [δ_{exp}] of incarcerated guests in [D$_{16}$]**4·1** and **4·9**, and of **9**, as well as predicted chemical shifts [δ_{pred}] for free **1**.

	[D$_{16}$]**4·1**	**4·9**	**9**	**1**
	δ_{exp}	δ_{exp}	δ_{exp} ($\Delta\delta$)[a]	δ_{pred}[b]
H1/H1′	3.76	3.19	5.39 (2.20)	5.84
H2/H2′	3.26	3.67	6.22 (2.55)	5.34
H3/H3′	4.93	4.61	6.62 (2.01)	7.01
H4		0.7	2.27 (1.57)	

[a] $\Delta\delta = \delta_{exp}(\mathbf{9}) - \delta_{exp}(\mathbf{4\cdot9})$. [b] $\delta_{pred} = \delta_{exp}([D_{16}]\mathbf{4\cdot1}) + \Sigma\Delta\delta(Hi)/4$.

Table 2. ^{1}H-^{1}H coupling constants of **1**.[a]

	H1,H1′	H1,H2/H1′,H2′	H2,H3/H2′,H3′	H3,H3′
$J_{H,H}$	− 9.8 (0.5)	2.4 (0.5)	8.5 (0.2)	4.5 (0.2)

[a] The 95%-confidence limits are given in parentheses.

To confirm our conclusion, we subjected **4·1** to different bulk phase reactants that can pass through a portal of **4** and that would lead to isolatable hemicarceplexes. Saturating a solution of **4·1** with HCl gas afforded instantaneously **4·**7-chlorocyclohepta-1,3,5-triene (**10**). Subsequent addition of methanol gave **4·**7-methoxycyclohepta-1,3,5-triene (**11**) (Scheme 1), evident from the characteristic singlet of the guest methyl protons at $\delta = -0.85$. We confirmed the formation of the latter hemicarceplex by comparison with authentic **4·11** which conclusively proved the successful phenylcarbene rearrangement to yield incarcerated **1**.[16] To our surprise, even after 3 h at 60 °C, the addition of methanol (5 M) to a solution of [D$_{16}$]**4·1** in [D$_8$]toluene did not result in the formation of [D$_{16}$]**4·11** although methanol is small enough to undergo through-shell reactions, for example with **10**. Kirmse et al. showed previously that free **1** and **2** instantaneously yield 7-ethoxycyclohepta-1,3,5-triene if generated in ethanolic solution through the protonation of **2**.[4b] Hence, the inner phase reactivity of **1** differs strongly from its reactivity in the bulk phase. We explain our results with an extremely low reactivity of **1** towards methanol and a very unfavorable equilibrium between **1** and **2** in the nonpolar inner phase of **4**. As pointed out by Kirmse and Sluma,[4c] a polar reaction phase strongly stabilizes the dipolar singlet state of **2**. For the same reason, the carbon–chlorine bond of **10** has covalent character in the inner phase rather than ionic.[17]

Though unreactive towards alcohols, incarcerated **1** rapidly reacts with oxygen. Exposure of [D$_{16}$]**4·1** to atmospheric oxygen leads quantitatively to [D$_{16}$]**4·**benzene (Figure 1 d).[8] We made use of this quantitative transformation to obtain a spectrum of [D$_{16}$]**4·1** by spectral subtraction (Figure 1 e).

We have demonstrated that phenylcarbene can be ring-expanded to cycloheptatetraene, which is stable for weeks at ambient temperature when protected from dimerization by incarceration. This clearly proves the superiority of inner phases for the investigation of highly strained reaction intermediates. We anticipate that this methodology will allow us to measure the kinetics of enantiomerization of **1** inside a chiral hemicarcerand and to draw mechanistic conclusions from the scrambling of isotopically labeled cycloheptatetraenes.

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