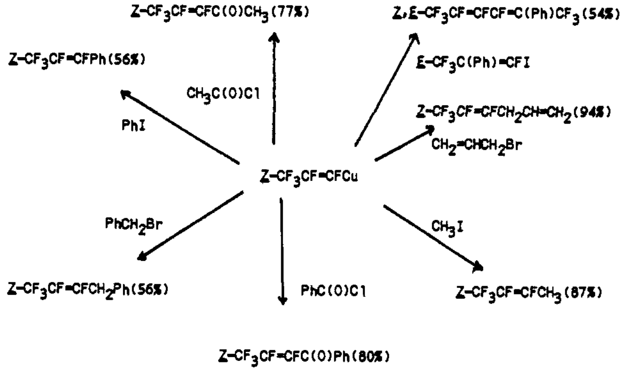
**Table I.** Preparation of Vinylcopper Reagents

| olefin | M | $R_FCF{=}CFCu$ | % yield[a] |
|---|---|---|---|
| $CF_2{=}CFI$ | Cd | $CF_2{=}CFCu$ | 99% |
| $CF_2{=}CFBr$ | Zn | $CF_2{=}CFCu$ | 72% |
| $(Z)$-$CF_3CF{=}CFI$ | Cd | $(Z)$-$CF_3CF{=}CFCu$ | 92% |
| $(Z)$-$CF_3CF{=}CFI$ | Zn | $(Z)$-$CF_3CF{=}CFCu$ | 76% |
| $(E)$-$CF_3CF{=}CFI$ | Cd | $(E)$-$CF_3CF{=}CFCu$ | 83% |
| $(Z)$-$CF_3(CF_2)_4CF{=}CFI$ | Cd | $(Z)$-$CF_3(CF_2)_4CF{=}CFCu$ | 87% |
| $(Z)$-$CF_3CCl{=}CFI$ | Cd | $(Z)$-$CF_3CCl{=}CFCu$ | 78% |
| $CF_3C(Ph){=}CFBr$<br>$E/Z = 59/41$ | Zn | $CF_3C(Ph){=}CFCu$<br>$E/Z = 59/41$ | 84% |
| $CF_3CF{=}C(Ph)CF{=}CFBr$<br>$E/Z = 90/10$ | Zn | $CF_3CF{=}C(Ph)CF{=}CFCu$<br>$E/Z = 90/10$ | 63% |

[a] Overall $^{19}F$ NMR yield based on starting olefin.

**Scheme I**[7]



a copper(I) halide metathesis reaction of the corresponding vinylcadmium and/or zinc reagents.[4] Table I summarizes these preliminary results.

$$\underset{X\,=\,Br,\,I}{R_FCF{=}CFX} + \underset{M\,=\,Cd,\,Zn}{M} \xrightarrow[\text{room temperature–60 °C}]{\text{DMF}} R_FCF{=}CFMX + (R_FCF{=}CF)_2M + MX_2 \xrightarrow[\text{room temperature}]{Cu^{I}X} \underset{68\text{–}99\%}{R_FCF{=}CFCu}$$

The preparation of the vinylcadmium or -zinc precursors proceeds stereospecifically, and the metathesis with $Cu^{I}X$ occurs with retention of configuration.[5] Consequently, stereochemical integrity is retained throughout the synthetic sequence and one can confidently prepare either isomeric copper reagent with total stereochemical control by proper choice of the appropriate vinyl halide.[6]

The vinylcopper reagents exhibit excellent stability at room temperature in the absence of oxygen and/or moisture. At higher temperature (>50 °C) they undergo rapid decomposition.

The vinylcopper reagents participate in a variety of alkylation, coupling, and acylation reactions as illustrated in Scheme I with $(Z)$-$CF_3CF{=}CFCu$.

The operational details of a typical experimental procedure for the pregeneration of $(Z)$-$CF_3CF{=}CFCu$ are outlined below: A two-necked 50-mL round bottom flask equipped with thermometer, magnetic stir bar, septum port, and condenser was charged under a nitrogen atmosphere with 6.5 g (0.025 mol) of $(Z)$-$CF_3CF{=}CFI$ and 25 mL of dry DMF. To this solution was added 3.5 g (0.031 mol) of acid-washed cadmium powder. After a short induction period, a mild exotherm resulted and a mixture of mono and bis $(Z)$-$CF_3CF{=}CFCdX$ was formed in 96% yield (mono/bis = 67/33) as determined by $^{19}F$ NMR. The excess cadmium was removed by pressure filtration under dry nitrogen through a fine fritted glass filter (Schlenk funnel). Then 4.2 g (0.029 mol) of CuBr was added to this mixture at 0 °C and the mixture was stirred for $^1/_2$ h followed by warming to room temperature. $^{19}F$ NMR analysis[8] indicated a 96% yield of $(Z)$-$CF_3CF{=}CFCu$. This solution was employed for subsequent functionalization reactions.

In summary, this work describes an *unequivocal* route to fluorinated vinylcopper reagents. The reagent is readily produced in situ from vinylic halides under mild conditions, is easily scaled up, allows total stereochemical control, and can be directly utilized in a wide variety of synthetic transformations. Our work continues with these reagents and future efforts will focus on the elucidation of the full scope of these new organometallic reagents.

**Acknowledgment.** We thank the National Science Foundation (CHE-85-16380) and the Air Force Office of Scientific Research (AFOSR-85-0009) for financial support of this work.

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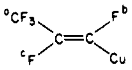
(4) Such reagents are prepared in 80–99% yield via direct reaction of cadmium or zinc powder with the corresponding vinyl iodide (at room temperature) or vinyl bromide (at 60 °C) in DMF.

(5) Stereochemical assignments are based on $J_{F,F}$ or $J_{F,CF_3}$ in either the organometallic reagent or in the reduced olefin $R_FCF{=}CFH$, obtained on hydrolysis of the copper reagent.

(6) In 1979 Miller and co-workers reported the preparation of $(E)$-$CF_3CF{=}C(CF_3)Cu$ from $(E)$-$CF_3CF{=}C(CF_3)Ag$: Miller, W. T. *Abstracts of the 9th International Symposium on Fluorine Chemistry*; Avignon, France; p 027. Our method avoids the use of the expensive silver intermediates and the problem of regiospecificity in the addition of AgF to a perfluoroalkyne.

(7) Yields in Scheme I are based on $^{19}F$ NMR using $PhCF_3$ as the internal standard.

(8) $^{19}F$ NMR of



exhibits the following spectroscopic parameters: $F_a$ (dd) −64.7, $F_b$ (dq) −135.9, and $F_c$ (dq) −180.0 ppm; $J_{ab} = 22.6$, $J_{ac} = 13.7$, and $J_{bc} = 100.2$ Hz.

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# New Cryptophane Forming Unusually Stable Inclusion Complexes with Neutral Guests in a Lipophilic Solvent

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In the absence of hydrophobic forces, host–guest complexes between uncharged species are usually weak[1-5] (stability constants $<\sim 10$ $M^{-1}$). We report here that new cavitand **2**, cryptophane E, can form inclusion complexes of comparatively very large

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[†] Equipe de recherche du C.N.R.S. No 285

(1) Very few complexes between *uncharged* host and guest partners in nonaqueous solvents have been reported; for relevant examples and general discussions, see ref 2–4 and the following papers: (a) Vögtle, F.; Müller, W. M. *J. Incl. Phenomena* **1984**, *1*, 369–386. (b) Jarvi, E. T.; Whitlock, H. W. *J. Am. Chem. Soc.* **1982**, *104*, 7196. Whitlock, B. J.; Whitlock, H. W. *J. Am. Chem. Soc.* **1985**, *107*, 1325–1329. (c) Bauer, L. J.; Gutsche, C. D. *J. Am. Chem. Soc.* **1985**, *107*, 6063–6069. (d) Mossier-Boss, P.; Popov, A. I. *J. Am. Chem. Soc.* **1985**, *107*, 6168–6174. (e) O'Krongly, D.; Denmeade, R.; Chiang, M. Y.; Breslow, R. *J. Am. Chem. Soc.* **1985**, *107*, 5544–5545.

(2) Moran, J. R.; Karbach, S.; Cram, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 5826–5828. Cram, D. J. *Science (Washington, D.C)* **1983**, *219*, 1177–1183. (b) Cram, D. J.; Stewart, K. D.; Goldberg, I.; Trueblood, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 2574–2575.

(3) **Cryptophane A**: Gabard, J.; Collet, A. *J. Chem. Soc., Chem. Commun.* **1981**, 1137–1139.

(4) **Cryptophane C and D**: (a) Canceill, J.; Lacombe, L.; Collet, A. *C. R. Acad. Sci., Ser. 2* **1984**, *298*, 39–42. (b) Canceill, J.; Cesario, M.; Collet, A.; Guilhem, J.; Pascard, C. *J. Chem. Soc., Chem. Commun.* **1985**, *361*–363. (c) Canceill, J.; Lacombe, L.; Collet, A. *J. Am. Chem. Soc.* **1985**, *107*, 6993–6996. (d) Canceill, J.; Cesario, M.; Collet, A.; Guilhem, J.; Riche, C.; Pascard, C. *J. Chem. Soc., Chem. Commun.* **1986**, 339–341.

(5) Water-soluble, cationic cyclophane hosts can form strong inclusion complexes with neutral aromatic hydrocarbons in aqueous solvents: (a) Diederich, F.; Griebel, D. *J. Am. Chem. Soc.* **1984**, *106*, 8037–8046. Diederich, F.; Dick, K. *Chem. Ber.* **1985**, *118*, 3817–3829. (b) Odashima, K.; Itai, Y.; Arata, Y.; Koga, K. *Tetrahedron Lett.* **1980**, *21*, 4347–4350. Soga, T.; Odashima, K.; Koga, K. *Tetrahedron Lett.* **1980**, *21*, 4351–4354. For a discussion of *hydrophobic effects*, see also: (c) Hashimoto, S.; Thomas, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 4655–4662.

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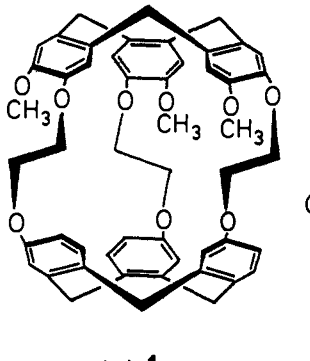
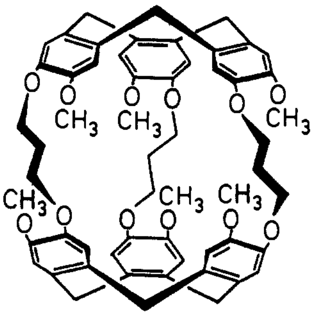
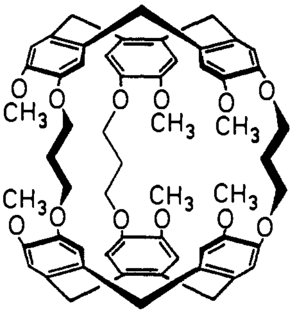
stability (>$10^2$ $M^{-1}$ at 300 K) with $CHCl_3$ and other halomethanes in $(CDCl_2)_2$.

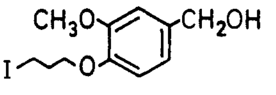
The cryptophanes[3,4] are well suited for inclusion of molecules of various sizes and shapes, because simple structural modifications of the host may produce stepwise changes in the dimensions of the cavity. For instance, CPK models indicate that in cryptophane C (**1**) the three $OCH_2CH_2O$ bridges give the cavity the volume of a $CHCl_3$ model, whereas experimentally[4] this host shows a marked preference for $CH_2Cl_2$ over smaller or bulkier guests. We have synthesized **2**, with three $OCH_2CH_2CH_2O$ bridges, in order to study the effect of a slight increase of the cavity volume on the complexation properties; models now suggest $CCl_4$ as being the ideal guest for **2**.

Cyclization precursor (±)-**5** (glass), obtained in 36% yield[6] from (±)-**6**[7] and **4**, was nearly quantitatively converted into a 4:6 mixture of isomers **2** and **3** by heating a $5 \times 10^{-4}$ M solution in $HCO_2H$ (60 °C, 3 h). Chromatographic workup[8] afforded **2** (27%, faster running) and **3** (50%), both crystalline, high-melting solids (mp >300 °C) showing expected mass ($M^+$ $m/z$ 937) and NMR spectra.[9] The *dl* ($D_3$) and *meso* ($C_{3h}$) structures were assigned to **2** and **3**, respectively, because optically active (−)-**5**, $[\alpha]^{25}_D$ −43° ($CHCl_3$), on reaction with $HCO_2H$ similarly afforded (+)-**2**, $[\alpha]^{25}_D$ +49°, and **3** for which no rotation could be measured. As (−)-**5** was prepared from known[10] (*M*)-(+)-**6** (>95% ee), the absolute configuration of **2** was established as shown on the formula.

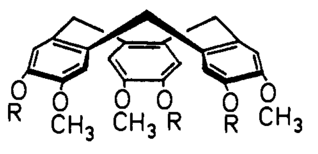

(−) 1


(+) 2


3



4 (= I—Z)



*P*(−) 5 R = Z

*M*(+) 6 R = H

In contrast to **3** which was sparingly soluble in all usual solvents, **2** was soluble in $CH_2Cl_2$, $CHCl_3$, and $CHBr_3$ and evaporation of the solutions yielded crystals with two molecules of solvent per host.[11] The $^1H$ NMR spectrum of the $CHCl_3$ complex in $(CDCl_2)_2$ at 300 K (Figure 1) and saturation transfer experiments revealed a slow exchange, on the 200-MHz spectrometer time scale, between the *free* and *complexed* $CHCl_3$ resonances, at $\delta_0$ 7.28 and $\delta_\infty$ 2.84. On heating, these signals broadened, as the inclusion/exclusion process became faster, and vanished above ~360 K (the fast exchange $CHCl_3$ peak could not be reached due to temperature limitation); cooling the sample down to 300 K restored the original spectrum. The huge upfield shift ($\Delta\delta$ 4.44) induced on the $CHCl_3$ resonance is consistent with an intramolecular inclusion of this guest in the cavity of **2** ("cavitate"). Thus **2** complexes reversibly $CHCl_3$ in $(CDCl_2)_2$, and the apparent[12] stability constant of the **2**·$CHCl_3$ cavitate in this solvent was estimated from the appropriate peak areas to be $K'_s$ 470 $M^{-1}$ (±10%) at 300 K. From the line shape of the exchanging $CHCl_3$ peaks, the barriers for entrance and departure of the guest were evaluated (±0.5 kcal/mol) to be $\Delta G^{\ddagger}$ (300 K) 13.4 and 17.2 kcal/mol, respectively. The plot of ln $K'_s$ vs. $1/T$ in the range 297–330 K gave ($r$ 0.996) $\Delta H$ −6.9 kcal/mol and $\Delta S$ −11 cal/(mol K); complexation of $CHCl_3$ by **2** is thus strongly enthalpy driven while it is entropy disfavored. A similar behavior has been reported[2b] for a bowl-shaped cavitand complexing $CS_2$ in $CDCl_3$, although the cavitate stability was much weaker (13.2 $M^{-1}$ at 250 K).

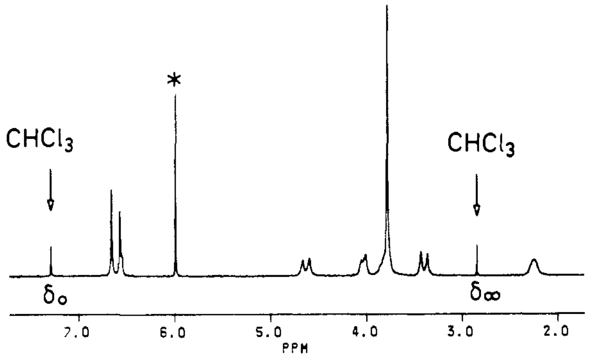


**Figure 1.** High-field 200.13-MHz $^1H$ NMR spectrum of **2** (0.01 M) and $CHCl_3$ (0.02 M) in $(CDCl_2)_2$ at 300 K; the star indicates the residual $Cl_2CHCDCl_2$ solvent peak. The host resonances are broadened as a consequence of the slow exchange between complexed and uncomplexed species having slightly different chemical shifts. The sharpness of the two $CHCl_3$ peaks is due to the large chemical shift difference ($\delta_0 - \delta_\infty$ 890 Hz) of the free and complexed guest species with respect to the exchange rate (ca. 2.5 $s^{-1}$).

Similar experiments with the $CH_2Cl_2$ and $CHBr_3$ complexes yielded, at 300 K, the following values of $K'_s$ (and $\delta_0 - \delta_\infty$): **2**·$CH_2Cl_2$ ~100 $M^{-1}$ (4.15); **2**·$CHBr_3$ ~40 $M^{-1}$ (4.36). Acetone, benzene, and ethanol were weakly complexed. Addition of 1 equiv of $CCl_4$ to the **2**·$CHCl_3$ complex in $(CDCl_2)_2$ did not detectably change the free/complexed $CHCl_3$ peak ratio; only a 20-fold excess of $CCl_4$ slightly decreased this ratio; hence the **2**·$CCl_4$ cavitate must be perhaps 2 orders of magnitude weaker than the $CHCl_3$ one.

The apparent stability ($K'_s$) of the cavitates not only depends on the intrinsic stability of the host–guest supermolecules but also encompasses *solvent–guest* and *solvent–host* interactions. The latter are probably unimportant here as the solvent seems too bulky to compete with the guest. Moreover, neither solvophobic nor solvophilic forces are likely to contribute to $K'_s$ significantly, since guest, host cavity, and solvent all are essentially lipophilic in character. When the guest is transferred from the bulk of the solvent to the host interior, the cavitation free energy for dissolution is released[13] ($\Delta G_c < 0$), whereas no extra cavitation energy (>0)

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(6) For a similar reaction, see ref 4c.

(7) Canceill, J.; Collet, A.; Gottarelli, G. *J. Am. Chem. Soc.* **1984**, *106*, 5997–6003.

(8) Cage isomers **2** and **3** showed very different $R_f$ values with the following eluents on silica gel: $CH_2Cl_2$/acetone 9:1 ($R_f$ 0.47 and 0.05); $CH_2Cl_2$/acetone 8:2 ($R_f$ 0.86 and 0.08); $CHCl_3/CH_3OH$ 95:5 ($R_f$ 0.84 and 0.52).

(9) Mass spectra taken at 70 eV on a ZAB-HF instrument, $^1H$ NMR spectra on a Bruker AM200SY spectrometer.

(10) Canceill, J.; Collet, A.; Gabard, J.; Gottarelli, G.; Spada, G. P. *J. Am. Chem. Soc.* **1985**, *107*, 1299–1308.

(11) As was observed[4] in cryptophane C and D, one of the solvent molecules is probably trapped in the host cavity and the other in voids of the lattice. The crystalline complexes of **2** turned out to be very stable and were not desolvated on prolonged heating (100–150 °C) under vacuum.

(12) Models suggest that this solvent could enter the host cavity to form a highly strained, hence probably very unstable, complex; in principle[4c] the true stability constant $K_s$ can be evaluated from $K'_s$ if the stability of the solvent–host complex is known.

is required to enter the preorganized host; therefore, as was already pointed out,[2b] $\Delta G_c$ should contribute to $K'_s$ favorably. However, this term, which depends on the guest volume, is expected to increase on going from $CH_2Cl_2$ to $CCl_4$, whereas the maximum stability is observed for the **2**·$CHCl_3$ complex. This fact probably means that the contribution of $\Delta G_c$ to the cavitate stabilization is relatively small. The high exothermal $\Delta H$ in the formation of the **2**·$CHCl_3$ cavitate is certainly best interpreted in terms of overall attractive host–guest interactions, which in this case should mainly consist of multipole–multipole and dispersion forces. As these interactions are strongly distance-dependent, we should conclude that effective *complementarity* between guest and host has been achieved in this complex. We simply observe that in **2** (and also in **1**), the best guest, experimentally, has a size substantially smaller than that suggested from examination of CPK models. Moreover, complementarity seems to be a very sharp requirement, if we consider that the **2**·$CHCl_3$ cavitate is stabler than the $CH_2Cl_2$ and $CHBr_3$ ones by $\Delta G \sim 1.0$ and 1.4 kcal/mol, respectively.

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(13) Cavity formation in solvents: see, for example: Stien, M. L.; Reisse, J. *Calorim. Anal. Therm.* **1984**, *15*, 214–219 and references therein.

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## Diadamantylcarbene in Solution[1]

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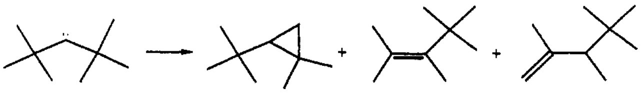
*Received October 15, 1985*
*Revised Manuscript Received April 28, 1986*

One of the substantial achievements of carbene chemistry has been the differentiation of singlet and triplet reactions. Diarylcarbenes have been the most often used vehicles for this work[6] although the parent methylene[6b] and carboalkoxycarbenes[7] have also found use. Conspicuously absent are alkyl- and dialkylcarbenes and for good reason: their chemistry is most one-sided. The reactive singlet states are effectively trapped by the available intramolecular reactions and the reactions of the lower energy, generally ground state, triplets are rendered invisible. Even when entry to the singlet–triplet manifold is gained through the triplet by photosensitized irradiation of a precursor, the reactions of the less stable singlet often win out.[6,7]

Triplet di-*tert*-butylcarbene has been observed by Gano and his collaborators[8] at 14 K. Workup produced 80% of **1** and **2**,



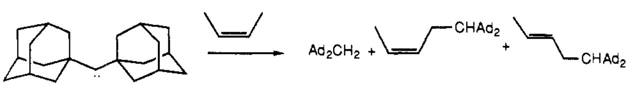
**1** **2** **3**

typical products of singlet carbene reactions, but the remaining 20% (**3**) was reasonably, if tentatively, attributed to the incursion of triplet carbene. Analysis of the zero-field parameters revealed a carbene surprisingly similar to methylene as the central bond angle was ca. 143° (triplet $:CH_2 = 137°$).[9] One must always bear in mind that the determination of angles from zero-field splitting parameters alone is not very reliable.

We have found that diadamantylcarbene (**4**) not only is a triplet ground state with a wider central angle than di-*tert*-butylcarbene but shows substantial triplet reactivity even in solution at 25 °C.

Irradiation of diadamantyldiazomethane[10] labeled with $^{13}C$ at the central position with an unfiltered 1000-W Hg-Xe lamp at 14 K produced a persistent triplet spectrum. Curie law analysis proved the triplet to be the ground-state species. The $^{13}C$ hyperfine splitting could be observed and related to the central angle by using the model of Brandon et al.[11] The hyperfine components of the high-field X and Y transitions and low-field Z transition are 252, 258, and 134 MHz, respectively. This compared with 282, 281, and 177 MHz for methylene.[12] Triplet diadamantylcarbene is long-lived in ethanol matrices between 4 and 75 K. In this respect it is even less reactive than diphenylcarbene. These values lead to a value of 152°, substantially wider than that in methylene[12] and essentially the same as that in diphenylcarbene.[11] A somewhat smaller angle of 146° can also be determined. At the suggestion of a referee we have analyzed the data by taking as the isotropic hyperfine interaction the average of the anisotropic hyperfine interactions oriented along the axes of the three zero-field transitions measured in our EPR experiment.[12a] If one assumes that one of the carbene orbitals is pure 2p (?) and the other an sp hybrid, the fractional s character of the hybrid orbital can be determined by using the correlation of either Higuchi[13a] or Harrison.[13b] We suspect that the bond angle in di-*tert*-butylcarbene, reported to be 143°,[8] is really larger as the zero-field parameters of **4** ($D/hc = 0.6823$ cm$^{-1}$, $E/hc = 0.038$ cm$^{-1}$) are nearly identical with those of di-*tert*-butylcarbene ($D/hc = 0.689$ cm$^{-1}$, $E/hc = 0.039$ cm$^{-1}$).[8]

Irradiation of dry, degassed[14] solutions of diadamantyldiazomethane in *cis*-2-butene at room temperature with a Hanovia medium-pressure mercury arc led to diadamantylmethane (**5**) as the major product (16% yield, 81% relative yield). The structure was confirmed by comparison with published data[10] although the position of the central methylene protons is not reported in the literature.[10] We have confirmed the unusually high upfield position of these protons (δ 0.9) by synthesizing deuterio-**5** from α-deuteriodiadamantylcarbinyl chloride. Small amounts of 1:1 adducts (4% yield, 19% relative yield) are also produced from **4** and *cis*-2-butene. The structures are tentatively assigned as **6** and **7** on the basis of their mass and $^1H$ NMR spectra.



**4** = $Ad_2C:$ **5** **6** **7**

Diadamantylmethane is surely a product of triplet carbene. Abstraction products are not reported for singlets[6b] but have been

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[1] Support from the National Science Foundation through Grants CHE-8318345 (Princeton) and CHE-8210710 (Ohio State) is gratefully acknowledged. Reactions of diadamantylcarbene in the gas phase have already been described: Sellers, S. F.; Klebach, T. C.; Hollowood, F.; Jones, M. Jr.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 5492.

[2] Garden State Fellow, 1980–1984.

[3] Princeton University.

[4] The Ohio State University.

[5] Camille and Henry Dreyfuss Fellow.

[6] (a) Griller, D.; Hadel, L.; Nazran, A. S.; Platz, M. S.; Wong, P. C.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 2227. Grasse, P. B.; Brauer, B.-E.; Zupancic, J. J.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 6833. (b) For general discussions of this problem see the chapters on carbene chemistry in Reactive Intermediates; Wiley: New York, 1978, 1981, 1985; Vols. 1, 2, 3.

[7] Gallucci, R. R.; Jones, M., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 7704.

[8] Gano, J. E.; Wettach, R. H.; Platz, M. S.; Senthilnathan, V. P. *J. Am. Chem. Soc.* **1982**, *104*, 2326.

[9] Leopold, D. G.; Murray, K. K.; Lineberger, W. C. *J. Chem. Phys.* **1984**, *81*, 1048 and references therein.

[10] Wieringa, J. H.; Wynberg, H.; Strating, J. *Tetrahedron* **1974**, *30*, 3053. Firouzabadi, H.; Ghaderi, E. *Tetrahedron Lett.* **1978**, 839. Hughey, J. L., IV; Knapp, S.; Schugar, H. *Synthesis* **1980**, 489. Slusarek, W., private communication.

[11] Brandon, R. W.; Closs, G. L.; Davoust, C. E.; Hutchison, C. A., Jr.; Kohler, B. E.; Silbey, R. *J. Chem. Phys.* **1965**, *43*, 2006.

[12] (a) Wasserman, E.; Kuck, V. J.; Hutton, R. S.; Anderson, E. D.; Yager, W. A. *J. Chem. Phys.* **1971**, *54*, 4120. (b) Bernheim, R. A.; Bernard, H. W.; Wang, P. S.; Wood, L. S.; Skell, P. S. *J. Chem. Phys.* **1971**, *54*, 3223.

[13] (a) Higuchi, J. *J. Chem. Phys.* **1963**, *39*, 1339. (b) Harrison, J. F. *J. Chem. Phys.* **1971**, *54*, 5413.

[14] Heroic measures are needed to eliminate water, which leads to diadamantylcarbinol, and, especially, oxygen, which leads to diadamantyl ketone. In this respect **4** strongly resembles diphenylcarbene.[15]

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