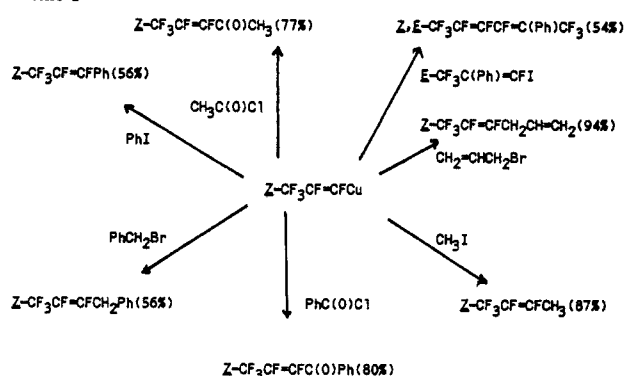
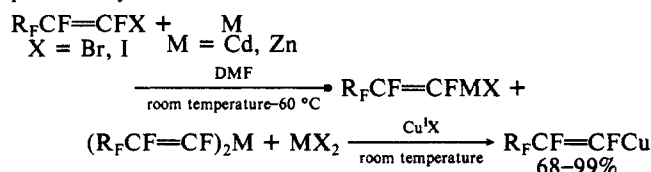


Table I. Preparation of Vinylcopper Reagents

olefin	M	R _F CF=CFCu	% yield ^a
CF ₂ =CFI	Cd	CF ₂ =CFCu	99%
CF ₂ =CFBr	Zn	CF ₂ =CFCu	72%
(Z)-CF ₃ CF=CFI	Cd	(Z)-CF ₃ CF=CFCu	92%
(Z)-CF ₃ CF=CFI	Zn	(Z)-CF ₃ CF=CFCu	76%
(E)-CF ₃ CF=CFI	Cd	(E)-CF ₃ CF=CFCu	83%
(Z)-CF ₃ (CF ₂) ₄ CF=CFI	Cd	(Z)-CF ₃ (CF ₂) ₄ CF=CFCu	87%
(Z)-CF ₃ CCl=CFI	Cd	(Z)-CF ₃ CCl=CFCu	78%
CF ₃ C(Ph)=CFBr	Zn	CF ₃ C(Ph)=CFCu	84%
E/Z = 59/41		E/Z = 59/41	
CF ₃ CF=C(Ph)CF=CFBr	Zn	CF ₃ CF=C(Ph)CF=CFCu	63%
E/Z = 90/10		E/Z = 90/10	

^a Overall ¹⁹F NMR yield based on starting olefin.Scheme I⁷

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



The preparation of the vinylcadmium or -zinc precursors proceeds stereospecifically, and the metathesis with Cu^IX 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)-CF₃CF=CFCu.

The operational details of a typical experimental procedure for the regeneration of (Z)-CF₃CF=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)-CF₃CF=CFI and 25 mL of dry DMF. To this solution was added 3.5 g (0.031 mol) of acid-washed cadmium powder. After

(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_{FF} or J_{FCF} 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)-CF₃CF=C(CF₃)Cu from (E)-CF₃CF=C(CF₃)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 regioselectivity in the addition of AgF to a perfluoroalkyne.

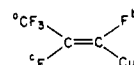
a short induction period, a mild exotherm resulted and a mixture of mono and bis (Z)-CF₃CF=CFCdX was formed in 96% yield (mono/bis = 67/33) as determined by ¹⁹F NMR. The excess cadmium was removed by pressure filtration under dry nitrogen through a fine fritted glass filter (Schlenk funnel). Then 4.2 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. ¹⁹F NMR analysis⁸ indicated a 96% yield of (Z)-CF₃CF=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.

(7) Yields in Scheme I are based on ¹⁹F NMR using PhCF₃ as the internal standard.

(8) ¹⁹F 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.

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 weak¹⁻⁵ (stability constants <~10 M⁻¹). We report here that new cavitand **2**, cryptophane E, can form inclusion complexes of comparatively very large

[†] 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.

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

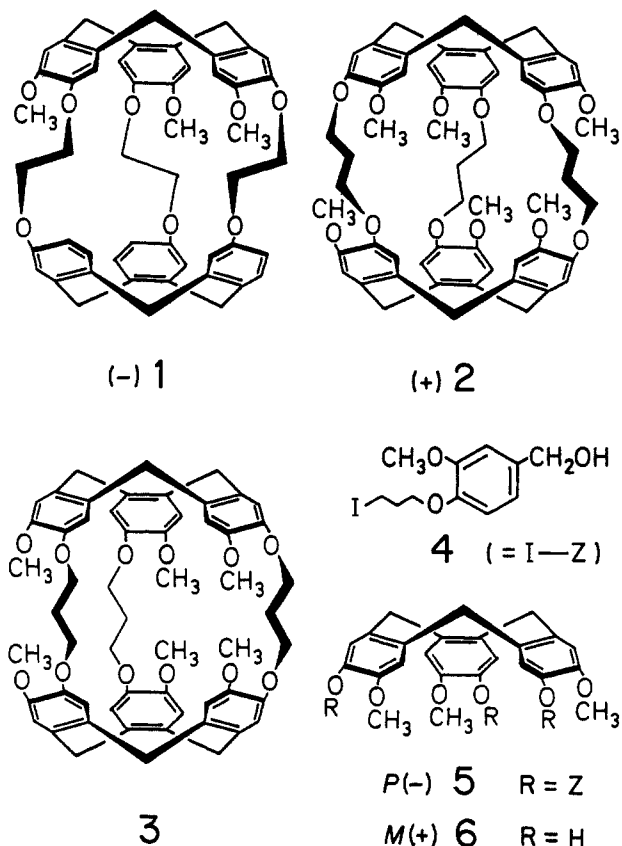
(4) Cryptophane C and D: (a) Canceill, J.; Lacombe, L.; Collet, A. *C. R. Acad. Sci., Ser. 2* **1984**, *298*, 39-42. (b) Canceill, J.; Cesario, M.; Collet, A.; Guilhem, J.; Pascard, C. *J. Chem. Soc., Chem. Commun.* **1985**, 361-363. (c) Canceill, J.; Lacombe, L.; Collet, A. *J. Am. Chem. Soc.* **1985**,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

stability ($>10^2 \text{ M}^{-1}$ at 300 K) with CHCl_3 and other halomethanes in $(\text{CDCl}_3)_2$.

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 $\text{OCH}_2\text{CH}_2\text{O}$ bridges give the cavity the volume of a CHCl_3 model, whereas experimentally⁴ this host shows a marked preference for CH_2Cl_2 over smaller or bulkier guests. We have synthesized **2**, with three $\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$ 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 (\pm)-**5** (glass), obtained in 36% yield⁶ from (\pm)-**6**⁷ and **4**, was nearly quantitatively converted into a 4:6 mixture of isomers **2** and **3** by heating a $5 \times 10^{-4} \text{ M}$ solution in HCO_2H (60 °C, 3 h). Chromatographic workup⁸ afforded **2** (27%, faster running) and **3** (50%), both crystalline, high-melting solids (mp $>300^\circ\text{C}$) 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**, $[\alpha]^{25}_D -43^\circ$ (CHCl_3), on reaction with HCO_2H similarly afforded (+)-**2**, $[\alpha]^{25}_D +49^\circ$, and **3** for which no rotation could be measured. As ($-$)-**5** was prepared from known¹⁰ (*M*)-(+)-**6** ($>95\%$ ee), the absolute configuration of **2** was established as shown on the formula.



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 $(\text{CDCl}_3)_2$

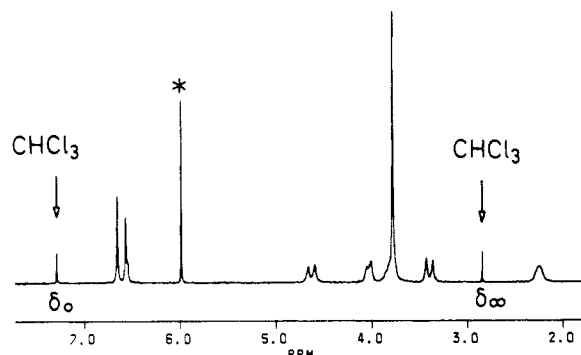


Figure 1. High-field 200.13-MHz ^1H NMR spectrum of **2** (0.01 M) and CHCl_3 (0.02 M) in $(\text{CDCl}_3)_2$ at 300 K; the star indicates the residual CHCl_3 solvent peak. The host resonances are broadened as a consequence of the slow exchange between complexed and uncomplexed species having slightly 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}).

Cl_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 δ_0 7.28 and δ_∞ 2.84. On heating, these signals broadened, as the inclusion/exclusion process became faster, and vanished above $\sim 360 \text{ K}$ (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 $(\text{CDCl}_3)_2$, and the apparent¹² 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} ($\pm 10\%$) at 300 K. From the line shape of the exchanging CHCl_3 peaks, the barriers for entrance and departure of the guest were evaluated ($\pm 0.5 \text{ kcal/mol}$) to be ΔG^\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) ΔH -6.9 kcal/mol and ΔS -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 cavitant complexing CS_2 in CDCl_3 , although the cavitate stability was much weaker (13.2 M^{-1} at 250 K).

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 $\sim 100 \text{ M}^{-1}$ (4.15); **2**- CHBr_3 $\sim 40 \text{ M}^{-1}$ (4.36). Acetone, benzene, and ethanol were weakly complexed. Addition of 1 equiv of CCl_4 to the **2**- CHCl_3 complex in $(\text{CDCl}_3)_2$ 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 released¹³ ($\Delta G_c < 0$), whereas no extra cavitation energy (>0)

(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: $\text{CH}_2\text{Cl}_2/\text{acetone}$ 9:1 (R_f 0.47 and 0.05); $\text{CH}_2\text{Cl}_2/\text{acetone}$ 8:2 (R_f 0.86 and 0.08); $\text{CHCl}_3/\text{CH}_3\text{OH}$ 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 observed⁴ 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} ΔG_c should contribute to K' , 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 ΔG_c to the cavitate stabilization is relatively small. The high exothermal ΔH 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.

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

Diadamantylcarbene in Solution¹

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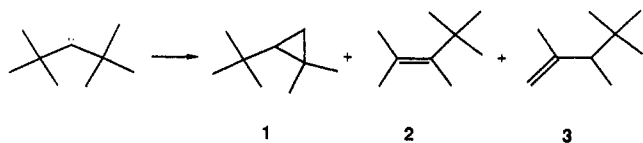
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One of the substantial achievements of carbene chemistry has been the differentiation of singlet and triplet reactions. Diarylcarbenes have been the most often used vehicles for this work⁶ although the parent methylene^{6b} and carboalkoxycarbenes⁷ 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 collaborators⁸ at 14 K. Workup produced 80% of **1** and **2**,



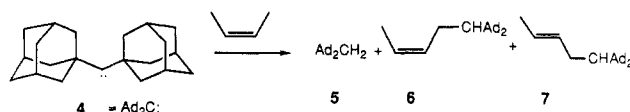
typical products of singlet carbene reactions, but the remaining 20% (**3**) was reasonably, if tentatively, attributed to the incursion

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 $:\text{CH}_2 = 137^\circ$).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 diadamantylidiazomethane¹⁰ 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 methylene¹² 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** ($D/hc = 0.6823\text{ cm}^{-1}$, $E/hc = 0.038\text{ cm}^{-1}$) are nearly identical with those of di-*tert*-butylcarbene ($D/hc = 0.689\text{ cm}^{-1}$, $E/hc = 0.039\text{ cm}^{-1}$).⁸

Irradiation of dry, degassed¹⁴ solutions of diadamantylidiazomethane 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 data¹⁰ 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 -deuteriodiadmantylcarbonyl 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.



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

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(2) Garden State Fellow, 1980-1984.

(3) Princeton University.

(4) The Ohio State University.

(5) Camille and Henry Dreyfuss Fellow.

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