(ZWO). We gratefully acknowledge valuable comments by the referees.

Registry No. **2a**, 101954-98-7; **2b**, 101954-99-8; **4a**, 101955-00-4; **4b**, 101955-01-5; **5a**, 101955-02-6; **5b**, 101955-03-7; **6a**, 101955-04-8; **6b**, 101955-05-9; **7a**, 37949-03-4; **7b**, 826-73-3; **8**, 97232-13-8; **9**, 54949-01-8; **10**, 101955-06-0; **12a**, 101955-07-1; **12b**, 101955-08-2; **17**, 952-80-7; **19**, 101955-09-3; **20**, 39110-21-9; **21**, 22927-13-5; **22**, 101955-10-6; **23**, 59659-68-6; **24**, 4748-78-1; **25a**, 101955-11-7; **25b**, 101955-12-8; **26**, 101955-13-9; **30**, 2628-17-3; **31**, 101979-24-2; (methoxymethylene)triphenylphosphorane, 20763-19-3; 6,7,8,9-tetrahydro-7-(methoxymethylene)-5*H*-benzocycloheptene, 101955-14-0; methylenetriphenylphosphorane, 3487-44-3; 2-methylbenzyl chloride, 552-45-4.

The Philicity of Fluorophenoxycarbene

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Fluorophenoxycarbene (FCOPh) was generated by thermolysis (50 °C) of 3-fluoro-3-phenoxydiazirine and added to six alkenes, affording the corresponding cyclopropanes. The substrates and relative reactivities were the following: tetramethylethylene (7.14), trimethylethylene (17.9), isobutene (14.3), 1-hexene (1.00), methyl acrylate (18.7), and acrylonitrile (33.6). The ambiphilic reactivity pattern of FCOPh resembles those of ClCOPh and ClCOMe. An ab initio study of FCOPh afforded geometries and frontier orbital energies for the cis and trans conformers of the carbene. Both conformers are predicted to be ambiphiles in alkene addition reactions, on the basis of simple frontier molecular orbital considerations.

One operational distinction between electrophilic, ambiphilic, and nucleophilic carbenes is based upon their differing selectivities toward olefinic substrates in the carbene/olefin cyclopropanation reaction.[1] *Electrophilic* carbenes add with increasing rate to alkenes of increasing π-electron richness (decreasing π-ionization potential); *nucleopilic* carbenes add with increasing rate to alkenes of decreasing π-electron availability (increasing π-ionization potential); *ambiphilic* carbenes exhibit a parabolic dependence on alkene π-electron availability that is characterized by high reactivity toward both electron-rich and electron-poor alkenes but low reactivity toward alkenes of intermediate electronic character.

This spectrum of carbenic reactivity can be understood in terms of frontier molecular orbital (FMO) interactions[1,2] and can be anticipated by estimation of the "carbene selectivity index," m_{CXY}.[1,3] Experimentally, m_{CXY} is defined (and measurable for electrophilic carbenes) as the least-squares slope of the correlation between log $(k_i/k_o)_{CXY}$ vs. log $(k_i/k_o)_{CCl_2}$, where the relative reactivities refer to the additions of the carbenes to a "standard" set of alkenes at 25 °C.[3] The observed dependence of m_{CXY} on the X and Y substituents of 9 carbenes, CXY, is correlated by eq 1, where $\sum_{X,Y}$ represents the sum of the appropriate substituent constants for X and Y, and m_{CCl_2} is set equal to unity.[1,3]

$$m_{CXY} = -1.10\sum_{X,Y}\sigma^+_R + 0.53\sum_{X,Y}\sigma_I - 0.31 \quad (1)$$

Using measured and calculated (from eq 1) values of m_{CXY}, we constructed a "carbene selectivity spectrum", locating carbenes according to the magnitude of m_{CXY}.[1,4] The resulting "spectrum" showed that experimentally nucleophilic carbenes, such as $(MeO)_2C$[5] and $MeOCNMe_2$,[6] had $m_{CXY} \gtrsim 2.2$, whereas typical electrophilic carbenes, such as CF_2,[7] had $m \lesssim 1.5$.[1,4] Thus, ambiphilic carbenes were expected to reside in the "intermediate" region of the selectivity spectrum; i.e., $1.5 \lesssim m_{CXY} \lesssim 2.2$.

Experiments subsequently demonstrated that both chloromethoxycarbene,[8-10] $m_{CXY}^{calcd} = 1.59$, and chlorophenoxycarbene,[11,12] $m_{CXY}^{calcd} = 1.49$,[11] did indeed behave as ambiphiles toward C=C-substituted alkenes and ring-substituted styrenes.

The known electrophilic carbene of highest m_{CXY}, CF_2[7] ($m_{CF_2}^{calcd} = 1.47$; $m_{CF_2}^{obsd} = 1.48$)[1] has a carbene selectivity index that is nearly identical with that of ClCOPh, so that the "border" between electrophilic and ambiphilic carbenes appears to lie a bit below 1.50. Where is the border between ambiphilic and nucleophilic carbenes? It must lie between 2.22, m_{CXY}^{calcd} for the nucleophilic dimethoxycarbene, and 1.59, m_{CXY}^{calcd} for the ambiphilic chloromethoxycarbene.

Recently, fluorophenoxydiazirine, a precursor for fluorophenoxycarbene (FCOPh), became available.[13] Using σ^+_R (PhO) = −0.87, σ^+_R(F) = −0.57, σ_I(PhO) = 0.38, and σ_I (F) = 0.50,[14] we can calculate from eq 1 that m_{CXY} = 1.74

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(8) Moss, R. A.; Fedorynski, M.; Shieh, W.-C. *J. Am. Chem. Soc.* **1979**, *101*, 4736. See also: Smith, N. P.; Stevens, I. D. R. *J. Chem. Soc. Perkin Trans. 2* **1979**, 1298.
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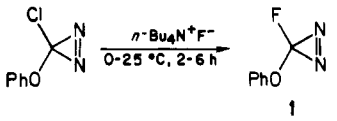
0022-3263/86/1951-2168$01.50/0

for FCOPh. This calculated carbene selectivity index is 0.15 unit higher than that of ClCOMe and correspondingly closer to that of the nucleophilic $(MeO)_2C$. The philicity of FCOPh is, therefore, of importance to our attempt to document the transition between ambiphilic and nucleophilic carbenic reactivity. Below, we characterize the philicity of FCOPh.

Results

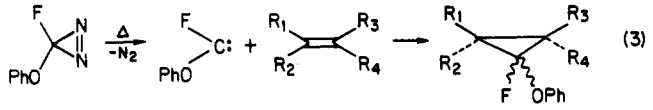
3-Fluoro-3-phenoxydiazirine (1) was prepared in 30–40% yield from 3-chloro-3-phenoxydiazirine by the exchange of fluoride for chloride, mediated by molten nearly anhydrous, tetra-*n*-butylammonium fluoride, eq 2.[13,15,16] The new diazirine was characterized by IR, UV, ^1H, ^{19}F, and ^{13}C NMR spectroscopy; details appear in the Experimental Section.



(2)

1

Cyclopropanes **2–7** were prepared by thermally decomposing diazirine **1** at 100–120 °C, 12–24 h (steel bomb), in excesses of tetramethylethylene, trimethylethylene, isobutene, 1-hexene, methyl acrylate, or acrylonitrile; eq 3.



(3)

2, $R_1=R_2=R_3=R_4=Me$
3, $R_1=R_2=R_3=Me$; $R_4=H$
4, $R_1=R_2=Me$; $R_3=R_4=H$
5, $R_1=n\text{-}C_4H_9$; $R_2=R_3=R_4=H$
6, $R_1=COOMe$; $R_2=R_3=R_4=H$
7, $R_1=CN$; $R_2=R_3=R_4=H$

The cyclopropanes were isolated by Kugelrohr distillation, with further purification by gas chromatography (GC) as appropriate. Isolated Kugelrohr yields ranged from 45% (**4**) to 8% (**5**). Mixtures of syn/anti isomers were obtained for cyclopropanes **3**, **5**, **6**, and **7**. These were not separated, but isomer distributions were determined by capillary GC. Product structures were subtantiated by ^1H NMR spectroscopy and by either elemental analysis or exact mass determination. However, configurations were not assigned to the syn and anti isomers. Further details appear in the Experimental Section.

The relative reactivities of FCOPh toward the several alkenes were determined by the competitive addition method.[17] The set of alkenes was designed and selected to reveal ambiphilic or nucleophilic carbenic properties[11] and included tetra-, tri-, di-, and monoalkylated ethenes as well as electron-deficient alkenes. Our older standard set of alkenes[3] did not contain either the electron-deficient alkenes or 1-hexene. Diazirine **1** was thermally decomposed (50 °C, 14 days, dark) in binary mixtures of excess alkenes.[18,19] The ratios of the product cyclopropanes were quantitatively determined by capillary GC using a flame ionization detector and an electronic integrator. The products were stable to the GC analytical conditions, and the detector was calibrated with known mixtures of cyclopropanes.

Table I. Experimental Relative Reactivities of FCOPh (50 °C)

case	olefin a	olefin b	k_a/k_b[a,b]
1	$Me_2C{=}CMe_2$	$Me_2C{=}CH_2$	$0.50 \pm 0.06_2$
2	$Me_2C{=}CHMe$	$Me_2C{=}CH_2$	$1.25 \pm 0.05_3$
3	$CH_2{=}CHCOOMe$	$Me_2C{=}CH_2$	$1.31 \pm 0.06_3$
4	$CH_2{=}CH\text{-}n\text{-}C_4H_9$	$Me_2C{=}CH_2$	$0.070 \pm 0.007_3$
5	$CH_2{=}CHCN$	$Me_2C{=}CH_2$	$2.35 \pm 0.05_2$
6	$CH_2{=}CHCN$	$Me_2C{=}CHMe$	$1.84 \pm 0.05_2$

[a] Where appropriate, relative reactivities are based on composites of syn and anti isomeric cyclopropane adducts. All analyses were by capillary GC (see below). [b] Errors are average deviations from the mean values of *n* (subscript) experiments.

Table II. Relative Reactivities of FCOPh and ClCOPh

olefin	FCOPh[a]	ClCOPh[b]
$Me_2C{=}CMe_2$	7.14	8.3
$Me_2C{=}CHMe$[c]	17.9	
$Me_2C{=}CH_2$	14.3	20.3
$CH_2{=}CH\text{-}n\text{-}C_4H_9$[c,d]	1.0	1.0
$CH_2{=}CHCOOMe$[c]	18.7	10.3
$CH_2{=}CHCN$[c]	33.6	15.3

[a] This work, 50 °C. [b] From ref 11, 25 °C. [c] The overall k_{rel} is the sum of both *syn*-PhO and *anti*-PhO additions of XCOPh to this olefin. [d] Standard olefin, k_{rel} = 1.0 by definition.

Yields were not routinely determined in the competition reactions because they were run on a very small scale (~100 mg of **1**). However, the competition reaction products were clean. No new products were observed by GC, and the major components were always the anticipated cyclopropanes. Control experiments indicated that typical competition product mixtures of the cyclopropanes (e.g., **7**/**4**, **3**/**4**, and **2** vs. a decane standard) were quantitatively stable to additional thermolysis at 50 °C for 14 days. For example, the GC peak area ratios before and after the additional heating were as follows: **7**/**4**, 0.62 vs. 0.66; **3**/**4**, 0.40 vs. 0.39; and decane/**2**, 0.66 vs. 0.68.

The relative reactivity of alkene a vs. alkene b was calculated from eq 4, where P_i is the (calibrated) mol

$$(k_a/k_b) = (P_a/P_b)(O_b/O_a) \quad (4)$$

fraction of product cyclopropane and O_i is the initial alkene mol fraction.[17] The experimentally determined relative reactivities toward FCOPh are recorded in Table I. Reproducibilities are generally better than ±5% of the mean value, save for cases 1 (12%) and 4 (10%). A cross-check experiment links cases 2, 5, and 6; from cases 2 and 6, we calculate $k(CH_2{=}CHCN)/k(Me_2C{=}CHMe)$ = 2.30, whereas the measured value (case 5) is 2.35, in excellent agreement.

We also examined the thermal decomposition (50 °C, 10 days) of diazirine **1** in 6,6-dimethylfulvene. However, no thermally stable products could be isolated; only a brown, viscous polymer was obtained. Note, however, that the regiospecificity of carbenic additions to dimethyl-

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(17) Review: Moss, R. A. In *Carbenes*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1973; Vol. I, p 153ff.
(18) Half-lives for the thermal decomposition of diazirine **1** were determined in decalin by following the disappearance of its UV absorptions at 340 and 356.5 nm. We observed ($\tau_{1/2}$, h; temperature, °C): 209, 40; 70, 50; 16, 60. Under the thermal conditions of the competition experiments (50 °C/14 days), about 5 half-lives were allowed for diazirine decomposition.
(19) Cyclopropane yields were superior when the diazirine was thermally, rather than photolytically, decomposed. Under the latter conditions, complex product mixtures containing little cyclopropane were obtained. The origin of this effect is still unclear, but may reflect particularly facile fragmentation of FCOPh when the carbene is generated from an excited state of the diazirine **1**. A similar problem is encountered with ClCOPh photogenerated from the chlorophenoxydiazirine.[20]
(20) Kesselmayer, M. A.; Sheridan, R. S. *J. Am. Chem. Soc.* **1986**, *108*, 844. We thank Professor Sheridan for a preprint of this work.

fulvene can differentiate electrophilic carbenes (that add to the endocyclic C=C) from ambiphilic or nucleophilic carbenes (that add to the exocyclic C=C),[10] but this test cannot differentiate ambiphilic from nucleophilic carbenes, and so it is not directly relevant to the present study.

Finally, although we did not make a detailed study of the stereospecificity of FCOPh, preliminary studies of the carbene's reactions with *cis*- and *trans*-pentene indicated no common cyclopropane products, suggesting that these additions were indeed stereospecific.

Discussion

In Table II, the experimental relative reactivities of FCOPh (Table I) are normalized to a 1-hexene standard and compared with analogous data for ClCOPh.[11] It is immediately clear that FCOPh behaves as an ambiphile toward the alkenes of this set and that its selectivity closely resembles those of ClCOPh[11] and ClCOMe.[8] The selectivity of these carbenes toward alkenes is described by a parabolic relation between relative reactivity and alkene "electron richness". These carbenes react rapidly with both the highly alkylated "nucleophilic" alkenes and the electron withdrawing group substituted "electrophilic" alkenes, whereas they react slowly with electronically intermediate alkenes such as 1-hexene.[21]

A quantitative response to the "geographical" question posed in the introduction to this paper can now be offered. The observed ambiphilicity of FCOPh indicates that the "border" between ambiphilic and nucleophilic carbenes must be located between $m_{CXY} = 1.74$ (FCOPh) and $m_{CXY} = 2.22$ [$(MeO)_2C$].

The origin of the ambiphilicity of singlet FCOPh[22] can be investigated with recourse to FMO theory. In particular, we are concerned with the interactions between the frontier molecular orbitals of the carbene and its alkene substrates.[1,2] We, therefore, carried out ab initio Hartree–Fock calculations on FCOPh on a DEC VAX 11/780 computer using the standard basis sets and methods available in the GAUSSIAN 82 series of programs.[23]

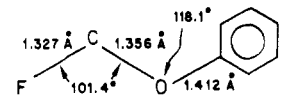
Matrix isolation studies of ClCOMe[24] and ClCOPh[20] indicate the presence of two carbene isomers, most likely cis and trans, that are configurationally stable at 10 K in argon or nitrogen matrices. We, therefore, directed our calculations toward several low-energy conformers of FCOPh, including the transition states for cis–trans isomerization and phenyl rotation. In all structures, the carbene's geometry including C–F, C–O, and O–C(Ph) bond lengths and FCO and COC bond angles was optimized with the minimal STO-3G basis set; the structure of the phenyl group was fixed, employing standard bond lengths and angles (C–C = 1.40 Å, C–H = 1.08 Å, all angles = 120°). Improved energies were subsequently obtained from single point calculations, at the optimized geometries, with the split valence 4-31G basis set. All energies quoted in the text were derived from calculations with the larger basis set. The entire procedure is analogous to previous work on related carbenes.[2,11]

Table III. Calculated Frontier Orbital Energies (eV) for XCOPh[a]

	carbene		
orbital	*trans*-ClCOPh	*trans*-FCOPh (8)	*cis*-FCOPh (9)
LUMO (p)[b]	2.02	2.56	3.17
HOMO (σ)	−10.78	−11.81	−11.78

[a] Energies are calculated at the 4-31G level for STO-3G optimized geometries; see text. [b] Note that there are two phenyl π orbitals energetically higher than the carbene σ orbital, but they are irrelevant for the present FMO considerations.

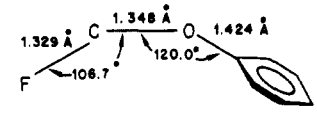
The most stable conformer of FCOPh is found to be the trans species 8 in which the phenyl group is coplanar with the FCO fragment. Where comparisons are valid, the optimized structure, detailed in 8, closely resembles the



8

structure previously calculated for *trans*-ClCOPh.[11] The phenyl group of 8 can freely rotate, because the energy of the otherwise optimized structure with phenyl perpendicular to the FCO plane is only 0.2 kcal/mol higher than the all-planar conformer.

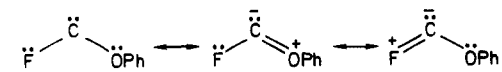
A secondary minimum for the FCOPh structure is the cis conformer 9 where the phenyl group is perpendicular to the FCO plane. Conformer 9 is calculated to be 3.8



9

kcal/mol higher in energy than 8. Rotation of the phenyl group in 9 is still relatively free, although the adiabatic barrier (1.4 kcal/mol) is larger than in 8 and arises from steric repulsions between the carbenic F and the ortho-H atoms of the phenyl group in the all-planar transition state for the phenyl rotation.

The transition state for the trans → cis conversion of 8 to 9 is 17.2 kcal/mol above the minium for 8 and was modeled by FCOPh with a 90° dihedral angle between FCO and COC(phenyl).[25] As in the cases of hydroxymethylene,[25] and of the ClCOMe and ClCOPh isomers observed at cryogenic temperatures,[20,24] the origin of this barrier is the partial C–O double bond (π-bond) character, illustrated for FCOPh in **10**. The double bond character arises from delocalization of an oxygen lone pair into the vacant carbenic π orbital (cf., **10b**) and is feasible *only* in FCOC-planar conformers 8 and 9



10a 10b 10c

Calculational support for this delocalization resides in the observation that the (F)C–O bond lengths in 8 and 9 are similar and ~0.05 Å shorter than the O–C(Ph) bond lengths, whereas in the transition state for 8 → 9 isomerization, these bond lengths are identical within 0.003 Å. That is, in the transition state, the carbenic carbon–oxygen

(21) We attribute the unusually low reactivity of FCOPh toward $Me_2C{=}CMe_2$ to a steric effect, as in the case of ClCOPh.[11]

(22) Triplet carbenes can also display ambiphilic selectivities. These can be understood in terms of the stabilities of the 1,3-diradicals that intervene in the triplet carbene/alkene addition reactions. Cf.: Tomioka, H.; Ohno, K.; Izawa, Y.; Moss, R. A.; Munjal, R. C. *Tetrahedron Lett.* **1984**, *25*, 5415.

(23) Binkley, J. S.; Frisch, M.; Raghavachari, K.; DeFrees, D. J.; Schlegel, H. B.; Whiteside, R. A.; Fluder, E.; Seeger, R.; Pople, J. A. Gaussian 82, Release H, Carnegie-Mellon University, Pittsburgh, PA, 1984.

(24) Kesselmayer, M. A.; Sheridan, R. S. *J. Am. Chem. Soc.* **1986**, *108*, 99. We thank Professor Sheridan for a preprint of this work.

(25) The corresponding calculated dihedral angle for the interconversion of *cis*- and *trans*-hydroxymethylene is 88°, and this transition state gives rise to a barrier of 27.5 kcal/mol for trans → cis isomerization: Goddard, J. D.; Schaefer, H. F. *J. Chem. Phys.* **1979**, *70*, 5117.

Table IV. Differential Orbital Energies for FCOPh/Alkene Additions

alkene	carbene and diffrntl orbtl energies (eV)[a]			
	trans-FCOPh (8)		*cis*-FCOPh (9)	
	p–π	π^*–σ	p–π	π^*–σ
Me_2C=CMe_2	10.83	14.08	11.44	14.05
Me_2C=CHMe	11.24	14.05	11.85	14.02
Me_2C=CH_2	11.80	14.00	12.41	13.97
CH_2=CH-*n*-C_4H_9[b]	12.08	13.80	12.69	13.77
CH_2=CHCOOMe	13.28	12.61	13.89	12.58
CH_2=CHCN	13.48	12.02	14.09	11.99

[a] For alkene π^* and π orbital energies see ref 1, 28, and 29. For carbene orbital energies, see Table III. [b] ϵ_{π^*} is approximated with the value for propene;[28] ϵ_{π} is approximated with the value for 1-pentene.[29]

delocalization is "turned off", and the (F)C–O bond "relaxes" to the same length as the O–C(Ph) bond. A similar result was calculated for the trans → cis isomerization of HO–CH.[25] It was also noted there[25] that the short C–O bond length (~1.34 Å) of the planar HOCH isomers (cf. 1.35–1.36 Å for **8** and **9**) is itself evidence for C–O π-bonding; a bond length of ~1.44-1.47 Å would be typical of a C–O single bond.

We should also note that the C–F bonds in **8** and **9** are calculated to be "short", ~1.33 Å. For comparison, the experimental C–F bond length of CF_2 is 1.30 Å.[26] Standard C–F bond lengths are 1.36 Å for the normal single bond and 1.33 Å for the C_{vinyl}–F bond.[27] Therefore, the calculated C–F bonds in the FCOPh conformers appear to be consistent with the partial C=F character expressed in **10c**.

The relevant frontier orbitals for FCOPh are the HOMO or σ and the LUMO or p orbitals. Calculated energies for these orbitals are shown in Table III, together with the analogous values previously calculated for trans-ClCOPh.[11] The replacement of Cl by F as we "convert" *trans*-ClCOPh to *trans*-FCOPh raises the carbene's LUMO energy and decreases its HOMO energy. Parallel effects were noted in the CCl_2, CFCl, CF_2 series[2] and can be rationalized by the better p–p overlap of F–C, relative to Cl–C (raising the LUMO energy), and the greater electronegativity of F, relative to Cl (lowering the HOMO energy). Comparison between the isomeric forms of FCOPh indicates that the HOMO energies are nearly equal, but that the LUMO of **9** is raised ~0.6 eV, relative to **8**.

In FMO analysis of carbene/alkene additions,[1,2] the quantities of interest are the transition state overlaps and the differential orbital energies of the carbene and alkene frontier orbitals; i.e., $LUMO_{carbene}$ with $HOMO_{alkene}$ and $LUMO_{alkene}$ with $HOMO_{carbene}$. The former term (p–π) represents *electrophilic* interaction of the vacant carbenic p orbital with the alkene π orbital; whereas the latter term (π^*–σ) measures *nucleophilic* interaction of the filled carbenic σ orbital with the vacant alkene π^* orbital. In general, carbenic electrophilicity is aided by a low-lying LUMO, whereas nucleophilic behavior is assisted by a high-lying HOMO. The replacement of Cl by F in going from ClCOPh to FCOPh raises the carbene's LUMO but also decreases the HOMO energy. These largely offsetting FMO effects lead us to anticipate similar overall philicities for FCOPh and ClCOPh.

Using the calculated p and σ carbene orbital energies of Table III and experimental alkene π^*[28] and π[29] energies, we estimate the *differential* carbene/alkene orbital energies collected in Table IV.

The transition-state geometry for the addition of FCOH to ethene has been calculated, and it was found that *both* p–π and σ–π^* carbene/alkene FMO overlap were significant.[2] Taking this result as also valid for the FCOPh/alkene additions of Table IV, we can qualitatively predict[1] the philicity of FCOPh. If a given carbene interacts with a set of alkenes so that the ($LUMO_{carbene}$ – $HOMO_{alkene}$) differntial energy is constantly less than that of ($LUMO_{alkene}$ – $HOMO_{carbene}$), then that carbene should manifest an electrophilic reactivity pattern with the set of substrate alkenes. An inverted relation of the differential orbital energies would predict that the carbene behave as a nucleophile toward the alkenes. Finally, a *crossing* of the differential orbital energies over the substrate set would predict ambiphilic reactivity.

The calculated differential orbital energies, for both FCOPh isomers, "cross over" in addition reactions to the alkenes of Table IV. There we see that the p–π interactions are characterized by lower differential energies than the π^*–σ interactions with alkylethylenes Me_2C=CMe_2, Me_2C=CHMe, Me_2C=CH_2, and *n*-BuCH=CH_2, whereas the reverse is true for electron withdrawing group substituted CH_2=CHCOOMe and CH_2=CHCN. FCOPh should react with the former alkenes in an electrophilic manner and with the latter alkenes as a nucleophile. Thus, FCOPh should behave as an ambiphile toward this set of alkenes, in accord with the experimental results of Table II.

FCOPh is thus seen to be an ambiphile in both the experimental reality and in predictions based upon simple (perhaps simplistic) applications of ab initio and FMO theory. In these properties, it is very similar to ClCOPh[11] and ClCOMe,[8] both predicted and observed to be ambiphiles, and distinct from the electrophilic CCl_2 and CF_2 or the nucleophilic $C(OMe)_2$. The philicities of these latter carbenes can also be rationalized by FMO considerations.[1]

There remains a final, but speculative observation. Although both *trans*-FCOPh and *cis*-FCOPh should be ambiphiles (Table IV), it is unclear that they would add equally well to a given alkene. Additions of *trans*-carbene **8** should be sterically more demanding than those of *cis*-carbene **9**, particularly with highly alkylated substrates such as Me_2C=CMe_2 or Me_2C=CHMe. Moreover, the **8** ⇌ **9** equilibrium is calculated to favor **8** by nearly 4 kcal/mol, and the **8** to **9** isomerization may be slow[30] relative to the rates of addition of carbenes in alkene solutions.[31] It is, therefore, conceivable that the rate-determining step in the addition of FCOPh to certain alkenes could be the trans to cis isomerization of the carbene, rather than the addition itself. For this to be so, however, the putative steric advantage of **9** over **8** would have to translate into at least several orders of magnitude in their respective addition rate constants.

Experimental Section

General Methods. Proton NMR spectra were recorded with either Varian T-60 or FT-80 spectrometers; solvents were $CDCl_3$

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(30) Assuming a preexponential factor of $\sim 10^{13}$–10^{14} s^{-1} and using the calculated E_a of ~17 kcal/mol (see above), we estimate that the rate constant for isomerization of **8** to **9** should be on the order of ~3–30 s^{-1} at 25 °C.
(31) Cf.: Gould, I. R.; Turro, N. J.; Butcher, J., Jr.; Doubleday, C., Jr.; Hacker, N. P.; Lehr, G. F.; Moss, R. A.; Cox, D. P.; Guo, W.; Munjal, R. C.; Perez, L. A.; Fedorynski, M. *Tetrahedron* **1985**, *41*, 1587.

or CCl_4, and chemical shifts are in δ units, relative to internal Me_4Si. Liquid alkenes and TBAF·$3H_2O$ were purchased from Aldrich Chemical Co. Isobutene was obtained from Matheson Co. Tetramethylethylene was distilled before use; other alkenes were used as received. Microanalyses were performed by Robertson Laboratory Florham Park, NJ.

3-Fluoro-3-phenoxydiazirine (1). Tetra-*n*-butylammonium fluoride trihydrate (TBAF·$3H_2O$), 10.0 g, was dried at 40–45 °C/0.005 mmHg until it had liquified and lost 17–21% of its initial weight.[15,16] To 8.42 g, ~32 mmol of this nearly anhydrous TBAF, contained in a round-bottomed flask, was added 3.00 g, 17.8 mmol, of 3-chloro-3-phenoxydiazirine.[11] The diazirine was added dropwise, while the TBAF was stirred magnetically and cooled in an ice bath. After the addition was complete, the reaction mixture was permitted to warm to room temperature. Stirring was continued, and the progress of the exchange reaction was monitored every 30 min by HPLC.[32] The exchange was continued until there was less than 10% of chlorodiazirine remaining (usually 2–6 h elapsed time); further reaction, or use of a larger excess of TBAF, led to product decomposition. The reaction product was diluted with ~40 mL of H_2O and the diazirine 1 was extracted with 4 × 20 mL of pentane. After drying ($MgSO_4$), the pentane was removed by distillation over a small Vigreux column, and the residue was distilled in a Kugelrohr apparatus at 25 °C/0.05 mmHg to afford 0.95 g (6.98 mmol), 39%, of pure fluorodiazirine 1: IR (neat, cm^{-1}) 1545 (s, N=N), 1270, 1195 (br s, CF and CO); UV (λ_{max}, nm, isooctane) 386 (ϵ 200), 350 sh, 339 (ϵ 183), 325 sh; ^1H NMR (δ, CCl_4) ~7.20 (m, aryl); ^{19}F NMR (δ, $CFCl_3$, $CDCl_3$) −116; ^{13}C NMR (δ, Me_4Si, $CDCl_3$) 86.7 (d, J^{13}_{CF} = 271 Hz, diazirine C).

Synthesis of Cyclopropanes. General Procedure. Diazirine 1 (3.0–6.5 mmol) was added to a cooled 100-mL metal bomb that contained 40–60 mmol of alkene (condensed at −78 °C in the case of isobutene) and a magnetic stirring bar. The bomb was sealed with a valve top and cooled to 77 K, and the contents were degassed, under vacuum, with two freeze–thaw cycles. The bomb was warmed to 25 °C, placed in an oil bath, and then heated to 100–120 °C for 12–24 h. The contents were stirred during heating. The bomb was then cooled to −78 °C and opened. Excess alkene was removed by evaporation (isobutene) or distillation on a Vigreux column. The residue was purified by Kugelrohr distillation, followed by preparative GC.[33]

1-Fluoro-1-phenoxy-2,2,3,3-tetramethylcyclopropane (2). This product was formed from diazirine 1 and tetramethylethylene in the metal bomb at 115 °C/20 h. It was isolated in 39% yield and purified by preparative GC[33] at 140 °C. The capillary GC retention time was 7.78 min: NMR (δ, CCl_4) 0.94 (d, J_{HF} = 2.5 Hz, 6 H, 2 Me), 1.17 (d, J_{HF} = 1.2 Hz, 6 H, 2 Me), 6.7–7.4 (m, 5 H, aryl). Anal. Calcd for $C_{13}H_{17}FO$: C, 74.97; H, 8.23; F, 9.12. Found: C, 74.84; H, 8.09; F, 8.90.

1-Fluoro-1-phenoxy-2,2,3-trimethylcyclopropanes (3). These isomeric compounds were formed from diazirine 1 and trimethylethylene in the metal bomb at 110 °C/20 h and in 32% yield. They were purified by preparative GC[33] at 135 °C. On capillary GC[33], the retention times of the isomers were 4.95 and 5.28 min, and their ratio was 1:10: NMR (δ, CCl_4, major isomer) 0.97–1.10 (m, 1 H, cyclopropyl), 1.13, 1.14 (d, J_{HF} = 1 Hz, 3 H, Me), 1.19, 1.21 (d, J = 2 Hz, 3 H, Me), 1.22 (d, J_{HF} = 1 Hz, 3 H, Me), 7.06–7.38 (m, 5 H, aryl). Anal. Calcd for $C_{12}H_{15}FO$: C, 74.19; H, 7.78; F, 9.78. Found: C, 73.99; H, 7.78; F, 9.61.

1-Fluoro-1-phenoxy-2,2-dimethylcyclopropane (4). This product was formed in 45% yield by reaction of diazirine 1 and isobutene in the metal bomb for 12 at 118 °C. It was purified by preparative GC[33] at 140 °C. The capillary GC[33] retention time was 3.05 min: NMR (δ, CCl_4) 0.73–0.97 (m, 2 H, cyclopropyl), 1.03 (d, J_{HF} = 3 Hz, 3 H, Me), 1.27 (d, J_{HF} = 2 Hz, Me); 6.6–7.4 (m, 5 H, aryl). Anal. Calcd for $C_{11}H_{13}FO$: C, 73.31; H, 7.27; F, 10.54. Found: C, 73.17; H, 7.25; F, 10.75.

1-Fluoro-1-phenoxy-2-*n*-butylcyclopropanes 5. These isomers were formed in 8% yield from reaction of diazirine 1 with 1-hexene in the metal bomb at 110 °C/24 h. They were purified by preparative GC[33] (twice) at 140 °C. Capillary GC[33] indicated two isomers with retention times of 12.15 and 14.20 min in a ratio of 1:1.2: NMR (δ, $CDCl_3$) 0.73–1.66 (m, 12 H, alkyl + cyclopropyl), 7.05–7.35 (m, 5 H, aryl); exact mass calcd for $C_{13}H_{17}FO$ 208.1263, found 208.1268.[34]

1-Fluoro-1-phenoxy-2-carbomethoxycyclopropanes 6. These isomers were formed in 20% isolated yield from diazirine 1 and methyl acrylate in the metal bomb for 24 h at 100 °C. The crude product was dissolved in acetonitrile and purified from polymeric methyl acrylate by passage through a short silica column. The cyclopropanes were purified by preparative GC[33] at 140 °C. Capillary GC[33] revealed two isomers with retention times of 8.75 and 13.44 min in a ratio of 1:1.1: NMR (δ, $CDCl_3$, mixture of isomers) 1.65, 1.85, 1.94, 2.20, 2.38, 2.60 (6 m's, 1 H each, cyclopropyl protons of each isomer), 3.57, 3.81 (2 s, 3 H each, OMe of each isomer), 7.07–7.20, 7.25–7.47 (2 m, 5 H each, aryls of each isomer). Anal. Calcd for $C_{11}H_{11}FO_3$: C, 62.85; H, 5.28; F, 9.03. Found: C, 62.65; H, 5.09; F, 9.38.

1-Fluoro-1-phenoxy-2-cyanocyclopropanes 7. These isomers were formed in 39% yield from diazirine 1 and acrylonitrile in the metal bomb at 115 °C for 12 h. They were purified by preparative GC[33] at 140 °C. Capillary GC[33] revealed two isomers with retention times of 6.89 and 8.57 min in a ratio of 1:1.4: NMR (δ, $CDCl_3$, mixture of isomers) 3 m's centered at 1.80, 2.00, and 2.35 (3 H, cyclopropyl), 7.09–7.39 (m, 5 H, aryl). Anal. Calcd for $C_{10}H_8FNO$: C, 67.79; H, 4.55; F, 10.72. Found: C, 67.61; H, 4.63; F, 10.99.

Competition Experiments. Diazirine 1 (1–2 mmol) was added to a screw-top Pyrex Carius tube containing a magnetic stirring bar and a carefully weighed binary mixture of the two alkenes, each present in at least 10-fold molar excess. The tube was sealed and covered with aluminum foil, and its contents were stirred magnetically at 50 °C (oil bath) for 14 days. The tube was cooled to −78 °C and opened, and the residue was analyzed by capillary GC. The results appear in Table I. Further methodology and relevant control experiments are presented in the Results section.

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Registry No. 1, 87282-21-1; 1 (3-chloro deriv.), 82849-43-2; 2, 87282-22-2; *cis*-3, 101860-42-8; *trans*-3, 101860-41-7; 4, 101860-43-9; *cis*-5, 101860-44-0; *trans*-5, 101860-45-1; *cis*-6, 101860-46-2; *trans*-6, 101860-47-3; *cis*-7, 101860-48-4; *trans*-7, 101860-49-5; $Me_2C{=}CMe_2$, 563-79-1; $Me_2C{=}CHMe$, 513-35-9; $Me_2C{=}CH_2$, 115-11-7; $H_2C{=}CHC_4H_9$, 592-41-6; $H_2C{=}CHCO_2Me$, 96-33-3; $H_2C{=}CHCN$, 107-13-1; fluorophenoxycarbene, 63707-33-5.

(32) We used a Waters HPLC with a C-18 reversed phase column and 254 nm UV detection. Solvents included 80/20 MeOH–water or 60/40 CH_3CN–water, both at 1 mL/min. Fluorodiazirine 1 eluted first in either solvent system.

(33) Preparative GC employed a 5 ft × 0.25 in. 20% SE-30 on 60/70 Anakrom ABS Teflon column. Analytical GC used a Varian Model 3700 flame ionization unit (injector, 250 °C, detector 300 °C, column 120 °C) fitted with a 12 m × 0.22 mm bonded-phase SE-30 vitreous silica capillary column. The typical N_2 flow rate was 25 mL/min.

(34) Exact mass determinations employed a VG Analytical 7070 EQ High Resolution mass spectrometer (Manchester, U.K.).