Selectivity of (Trifluoromethyl)chlorocarbene

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Abstract: (Trifluoromethyl)chlorocarbene (CF_3CCl) was generated by photolysis of 3-(trifluoromethyl)-3-chlorodiazirine and added to eight alkenes affording the corresponding cyclopropanes. Additions to *cis*- and *trans*-butenes were stereospecific. No allylic CH insertion products were observed with any of the substrates. Substrates, reactivities (relative to $Me_2C{=}CH_2$ = 1.00), and stereoselectivities (syn-Cl/anti-Cl) for the CF_3CCl addition reactions follow: $Me_2C{=}CMe_2$, 0.92, none; $Me_2C{=}CHMe$, 1.17, 1.48; $Me_2C{=}CH_2$, 1.00, none; *cis*-MeCH=CHMe, 0.88, 1.65; *trans*-MeCH=CHMe, 0.62, none; $EtCH{=}CH_2$, 0.48, 1.28; *i*-$PrCH{=}CH_2$, 0.25, 1.36; *t*-$BuCH{=}CH_2$, 0.11, 1.66. The reactivity data are analyzed and compared to analogous results for CH_3CCl and CCl_2. The carbene selectivity index, m_{CXY}, of CF_3CCl is $\sim$0.19 (m_{CCl_2} = 1.00), and its steric demand during addition to $RCH{=}CH_2$ (Taft δ) is 0.41 (δ_{CCl_2} = 0.88). Relative to CH_3CCl, CF_3 strongly destabilizes CF_3CCl. This conclusion follows both from analysis of the experimental data and from ab initio calculations. CF_3CCl is believed to add to alkenes via "early", relatively "open" transition states, in which electronic and steric selectivities are leveled.

The unique polar effects of the trifluromethyl (CF_3) group have focused much attention on this moiety as a useful probe substituent in mechanistic and spectroscopic investigations.[2] Much progress has been recorded in the areas of heterolytic and homolytic aromatic or aliphatic reaction chemistry,[2] but the influence of the CF_3 group on the reactivity of *carbenic* intermediates is poorly characterized from the quantitative standpoint.

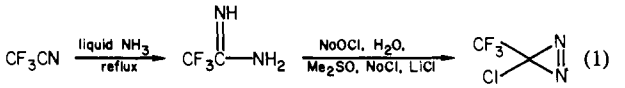
Bis(trifluoromethyl)carbene reacts with aromatic and aliphatic substrates, the latter including saturated and unsaturated examples,[3a-d] as well as with carbonyl fluoride (to give an oxirane)[3e] and with alkynes to yield cyclopropenes.[3f] In its reactions with *cis*-butene, *trans*-butene, and cyclohexene, $(CF_3)_2C$ appears to behave as a triplet,[3c] which is known to be the carbene's ground state.[4] Triplet involvement is also apparent in the nonstereospecific addition of (trifluoromethyl)carbene to *cis*-butene.[5] CF_3CH also possesses a triplet ground state,[4] but both singlet and triplets seemed to be involved in its reactions with hydrocarbons. The singlet inserts into CH bonds with very little selectivity, suggesting a destabilizing effect of CF_3 on a singlet carbenic center.[6] There are also references to reactions of (trifluoromethyl)cyanocarbene[7] and (trifluoromethyl)(carboethoxy)carbene,[8] but these reports do not focus on carbenic reactivity.

Generally, carbenes bearing halogen atoms directly bonded to the carbenic center are considerably more selective than related carbenes bearing hydrogen or electron-withdrawing substituents.[9] Accordingly, CF_3CHal should be much more amenable to a reactivity study than $(CF_3)_2C$ or CF_3CH. Members of the CF_3CHal class[10] include CF_3CF,[11] CF_3CCl;[12,13] a related species is CF_2HCF.[14] CF_3CF and CF_2HCF are usually generated by pyrolysis ($\sim$150 °C) of organometallic precursors.[11,14] Selectivity data collected under these conditions would not be directly comparable to the large body of selectivity data now available for other carbenes at 25 °C.[9,15] Similarly, CF_3CCl has been generated by pyrolysis of either $PhHg(CF_3)CBrCl$ (130-140 °C)[12] or 3-(trifluoromethyl)-3-chlorodiazirine (120 °C).[13] The latter precursor, however, should also be photochemically labile at 25 °C, making practical a selectivity study of CF_3CCl under mild and normative[9,15] reaction conditions.

Although the carbene-alkene addition reaction is the principal vehicle for the assessment of carbenic selectivity,[15] there are no selectivity studies of CF_3-substituted carbenes with simple alkenes. A study of CF_3CCl would bridge this gap and would also provide data directly comparable to analogous results for CH_3CCl.[16] A clear measure of the influence of the CF_3 group on carbenic selectivity would thus be obtained. We now present the first experimental and theoretical results from a study of CF_3CCl selectivity.

Results

3-(Trifluoromethyl)-3-chlorodiazirine (**1**)[13] was generated from trifluoroacetamidine[13,17] by hypochlorite oxidation[18] and condensed into pentane at 77 K (eq 1). Portions of the cold pentane solutions



(1)

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were diluted with various alkenes at −78 °C, and the dilute diazirine/alkene solutions were then photolyzed for 3 h (25-30 °C) in sealed tubes, using a focused Osram 200-W XE mercury lamp. Products were isolated by preparative GC after careful evaporation of the alkenes. Yields of the isolated cyclopropane products, based

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(17) Experimental details were supplied in a private communication from Professor D. M. Lemal (Dartmouth College). The details, for which we are grateful, appear in the Experimental Section.
(18) Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396.

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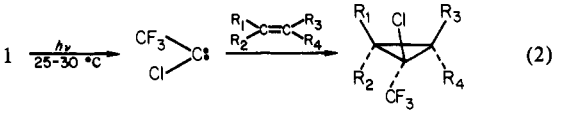
on trifluoroacetamidine, were quite low (2–12%), but the reactions were very clean. The alkenes used were tetramethylethylene, trimethylethylene, isobutene, *cis*-butene, *trans*-butene, 1-butene, isopropylethylene, and *tert*-butylethylene. These afforded cyclopropanes **2–9**, respectively, as shown in eq 2.

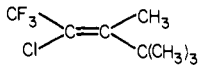


(2)

2, $R_1 = R_2 = R_3 = R_4 = Me$
3-syn-Cl, $R_1 = R_2 = R_3 = Me$, $R_4 = H$
3-anti-Cl, $R_1 = R_2 = R_4 = Me$, $R_3 = H$
4, $R_1 = R_2 = Me$, $R_3 = R_4 = H$
5-syn-Cl, $R_1 = R_3 = Me$, $R_2 = R_4 = H$
5-anti-Cl, $R_1 = R_3 = H$, $R_2 = R_4 = Me$
6, $R_1 = R_4 = Me$, $R_2 = R_3 = H$
7-syn-Cl, $R_1 = Et$, $R_2 = R_3 = R_4 = H$
7-anti-Cl, $R_2 = Et$, $R_1 = R_3 = R_4 = H$
8-syn-Cl, $R_1 = i\text{-Pr}$, $R_2 = R_3 = R_4 = H$
8-anti-Cl, $R_2 = i\text{-Pr}$, $R_1 = R_3 = R_4 = H$
9-syn-Cl, $R_1 = t\text{-Bu}$, $R_2 = R_3 = R_4 = H$
9-anti-Cl, $R_2 = t\text{-Bu}$, $R_1 = R_3 = R_4 = H$

Photolyses in trimethylethylene, *cis*-butene, and $RCH{=}CH_2$ (R = Et, *i*-Pr, *t*-Bu) led to the expected pairs of syn/anti isomers **3**, **5**, **7**, **8**, and **9**. The product structures were substantiated by ^1H and ^{19}F NMR spectra, elemental analysis, mass spectra, and comparisons with literature data for the known compounds **2**, **3**, **5**, and **6**.[12] Details of these observations appear in the Experimental Section; however, the differentiation of *syn/anti* isomers will be discussed below.

When CF_3CCl was generated from $PhHg(CF_3)CClBr$ (130 °C, 54 h) and added to $Me_2C{=}CMe_2$, cyclopropane **2** and olefin **10**



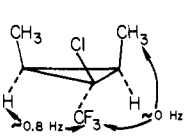
10

(tentative assignment) were obtained in 58% and 13% yields, respectively.[12] The olefin is most likely a thermal rearrangement product of **2**. Thus, we find that *photolysis* of **1** (30 °C, 3 h) in $Me_2C{=}CMe_2$ affords only cyclopropane **2**, although thermolysis (120 °C, 3 h) gives both **2** and **10** (NMR[12]) in a GC ratio of 9:1.

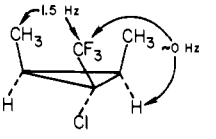
Stereospecificity. GC permitted the separation of *trans*-butene adduct **6** from isomeric *cis*-butene adducts **5** (conditions: 20 ft × $^3/_{16}$ in. 10% SE-30 on 80/100 Anakrom ABS column at 60 °C; injector, 140 °C; detector, 175 °C; He flow 80 mL/min). Addition of CF_3CCl (photolytically generated from **1**) to *cis*-butene gave only (≥99%) adducts **5**, whereas addition of CF_3CCl to *trans*-butene gave only (≥99%) adduct **6**. Control GC experiments demonstrated that 1% of **6** could be readily detected in 99% of **5**. The stereospecificity revealed in reactions of CF_3CCl with *cis*- or *trans*-butene suggests that *singlet*[19] CF_3CCl is the reactive form of the carbene observed under our reaction conditions. Stereospecific additions of CF_3CCl to *cis*- and *trans*-butenes were also observed upon thermolysis (135 °C, 10 days) of $PhHg(CF_3)CClBr$ in these alkenes.[12]

Stereoselectivity. CF_3CCl additions to alkenes which lacked both a center of symmetry and a twofold rotational axis coincident with the double bond afforded isomeric pairs **3**, **5**, **7**, **8**, and **9**. Excepting the trimethylethylene adducts (**3**), these were all separable by GC. Assignment of configurations, however, proved very difficult. The case of the *cis*-butene adducts (**5**) was intensively studied.

The two isomers, **5-syn-Cl** and **5-anti-Cl**, were formed in a 1.65:1 ratio (GC) and separated at 70 °C on a 19 ft × 0.25 in. 15% SF-96 on 80/100 Chromsorb W column. Under these conditions, the major product eluted first. At 60 MHz the ^1H NMR spectrum of "major" showed a crude doublet for the Me resonances at δ_{CCl_4}



5-syn-Cl



5-anti-Cl

1.10 and a multiplet for the ring protons centered at ~δ 1.53. "Minor" displayed its Me "doublet" and ring CH multiplet at δ 1.27 and 1.67, respectively. In the ^{19}F NMR spectra (Varian FT-80 spectrometer, equipped with a broad-band probe), major and minor isomers gave signals at 73.6 and 62.6 ppm *upfield* from an internal CCl_3F reference (in $CDCl_3$), respectively.[20]

We assign the major isomer the **5-syn-Cl** structure and the minor isomer the **5-anti-Cl** structure on the basis of the long range H–F couplings observed in their high-field ^1H and ^{19}F NMR spectra. There is strong evidence that long range H–F coupling is largely a "through-space" phenomenon, dependent on spatial proximity of the two nuclei.[21]

In the 300-MHz proton spectrum (Varian SC-300 spectrometer, $CDCl_3$) of **5-syn-Cl** (major), decoupling the ring CH protons reduced the Me resonance to a singlet; there was no ($J \leq 0.2$ Hz) long-range (anti) CF_3–CH_3 coupling. On the other hand, the ring CH protons of **5-syn-Cl** (with Me decoupled) displayed 0.8-Hz residual coupling to the (syn) CF_3 fluorines. These measurements were on 100-Hz width display, 300-MHz spectra, where 1 Hz = 5 mm. In the 188-MHz ^{19}F NMR spectrum (Varian XL-200 spectrometer), **5-syn-Cl** displayed the reciprocal 0.75-Hz HF coupling between CF_3 and ring CH atoms. The CF_3 fluorines appeared as a quintet, X_3 of $AA'X_3$.

In the 300-MHz proton spectrum of **5-anti-Cl** (minor), decoupling of the ring CH protons revealed the Me resonances to be a quartet with (syn) CH_3–CF_3 ($^5J_{HF}$) = 1.5 Hz. When the Me protons were decoupled and the ring CH protons were observed, however, there was no (≤0.2 Hz) detectable HF coupling. The 188-MHz ^{19}F NMR spectrum afforded the reciprocal 1.5-Hz H–F coupling between CH_3 and CF_3. The F resonance was a septet due to coupling to six equivalent methyl protons. The observed long-range coupling constants are summarized in the structural formulas above.

Significant long-range HF coupling between CF_3 and CH_3 or ring CH is observed only when CF_3 is syn to the particular proton or protons. In the sense that *syn*-CF_3–CH or *syn*-CF_3–CH_3 are the spatially proximate situations,[21] the observed couplings would appear to be consistent only with the suggested configurational assignments.[50]

The stereoselectivity of CF_3CCl addition to *cis*-butene is therefore preferentially syn-Cl (or anti-CF_3). In this, it behaves similarly to CH_3CCl, for which syn-Cl/syn-CH_3 stereoselectivity is 2.84:1 at 25–30 °C.[16] In both cases, the major mode of addition opposes the *smaller* (Cl) carbenic substituent to the *cis*-butene Me groups. The kinetically controlled stereoselectivities of CF_3CCl and CH_3CCl toward *cis*-butene appear to be mainly determined by relative steric hindrance between carbenic and olefinic substituents in the alternative syn-Cl or anti-Cl transition states.[22]

On the basis of steric control of CF_3CCl stereoselectivity, we tentatively assign the stereoselectivities of the other CF_3CCl addition reactions as indicated in Table I. The syn-Cl/anti-Cl ratios increase (albeit gently) as R in $RCH{=}CH_2$ increases in size. This is in accord with configurational assignments based on relative steric hindrance in kinetically competitive syn and anti transition states.

We must note, however, that these configurational assignments mean that all of the syn-Cl (anti-CF_3) cyclopropanes have *higher* field ^{19}F chemical shifts than their anti-Cl (syn-CF_3) isomers. (See the Experimental Section for ^{19}F chemical shifts.) This is

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(20) All ^{19}F chemical shifts in this paper are reported in parts per million upfield from internal CCl_3F in $CDCl_3$ solvent.

(21) Review: Hilton, J.; Sutcliffe, L. H. *Prog. NMR Spectrosc.* **1975**, *10*, 27.

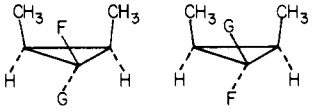
(22) A fuller discussion appears below.

Table I. Stereoselectivity of CF_3CCl Additions[a]

alkene	adducts	syn-Cl/ anti-Cl (syn-CF_3)[b]
Me_2C=CHMe	3	1.48[c]
cis-MeCH=CHMe	5	1.65
EtCH=CH_2	7	1.28
i-PrCH=CH_2	8	1.36
t-BuCH=CH_2	9	1.66

[a] At 25–30 °C; determined by GC analysis of crude reaction mixtures. The GC conditions are described below in the section on relative reactivity experiments. [b] Errors (% a.d.) in repetitive GC analyses were <3%. [c] By integration of the ^{19}F NMR spectrum of the crude product mixture.

somewhat surprising and contrary to expectations based on compounds such as **11** and **11′** (G = Cl[23] or Ph[24]), where syn-Me



11 **11′**

groups shield the syn-cyclopropyl fluorine of **11**, relative to the anti fluorine atom of **11′**. Structural assignments to **5** based on coupling constants thus force us to conclude that CF_3 (in place of F in **11**) is *deshielded* by syn-Me groups. We lack a good explanation for this phenomenon, but we feel that the long-range coupling[21] here constitutes a superior basis for configurational assignments than the less well-rationalized ^{19}F chemical shifts.

Relative Reactivity Experiments. Competitive additions of CF_3CCl in binary alkene mixtures were carried out in the usual way.[9] Diazirine **1** was photolyzed ($\lambda > 300$ nm) for 3 h in olefinic solutions (sealed tubes) at 30 °C. Each olefin was present in at least tenfold excess over **1**. Products were stable to the GC conditions selected for quantitative analysis, and the thermal conductivity detector was calibrated by using pure products. Relative reactivities for olefin a vs. olefin b were calculated from expression 3, where P_i is the mole fraction of product cyclopropanes

$$(k_a/k_b) = (P_a/P_b)(O_b/O_a) \quad (3)$$

and O_i is the initial mole fraction of olefins.[9] Experimentally determined relative reactivites are collected in Table II.

Discussion

Steric Selectivity. The stereoselectivity of CXY carbenic additions to (e.g.) *cis*-butene depends on the relative energies of the X/Me_2 and Y/Me_2 nonbonded interactions in the alternative syn-X and syn-Y transition states.[9,25] At appropriate internuclear separations, X/Me_2 interactions can be attractive due to van der Waals or London dispersion forces.[25] At large reactant separations, in the early transition states associated with highly exothermic reactions, these interactions may also be attractive due to in-phase secondary orbital interactions between carbenic and olefinic substituents ("steric attraction").[26] Of course, at sufficiently close separations, the X/Me_2 interaction will be net repulsive because of closed-shell repulsions between the carbenic and olefinic substituents ("steric hindrance").[25,26]

CF_3CCl exhibits syn-Cl (or anti-CF_3) stereoselectivity toward *cis*-butene with syn-Cl/anti-Cl = 1.65. This seems consistent with both electronic and steric expectations. Chlorine interacts attractively with syn-CH_3 groups in carbenic additions of ClCR to *cis*-butene. For example addition of ClCF to *cis*-butene is syn-Cl stereoselective,[23] although preferential syn-F addition might have been anticipated on the basis of relative steric hindrance (Cl > F). Dominant electrostatic attraction of the more polarizable Cl for the Me groups in the alternative addition transition states has been held responsible.[23,27] The additions of $ClCCH_3$,[16] $ClCC_6H_5$,[28] and ClC-cyclo-C_3H_5[29] to *cis*-butene are also syn-Cl stereoselective, although, in these latter cases, the greater steric demand of the second carbenic substituent (relative to Cl) must reinforce the syn-Cl-directing attractive forces.

We believe that syn-Cl addition of CF_3CCl to *cis*-butene is also buttressed by the smaller steric demand of Cl, relative to CF_3. The differential Taft steric substituent constant, ΔE_s ($=E_s^{CF_3} - E_s^{Cl}$) = −1.34, with CF_3 the sterically more demanding substituent.[30]

Although the stereoselectivity of CF_3CCl appears (perhaps deceptively) to be readily rationalized, comparison with the stereoselectivity of CH_3CCl presents a problem. The larger steric demand of CF_3, relative to CH_3 ($\Delta E_s = -1.16$),[30] suggests that CH_3CX should exhibit greater syn-CH_3 stereoselectivity (or at least *less* anti-CH_3 stereoselectivity) than would be observed for CF_3 in the corresponding reactions of CF_3CX. Indeed, it appears that CH_3CH adds to propene with a small syn-CH_3 preference (1.4:1),[31] whereas, under conditions where its addition to *cis*-butene is reasonably stereospecific, CF_3CH adds to propene with slight anti-CF_3 stereoselectivity (1.2:1).[32] We might therefore expect CH_3CCl to be *less* syn-Cl (i.e., more syn-CH_3) stereoselective than CF_3CCl. That is, CF_3CCl should exhibit greater anti-CF_3 stereoselectivity than the anti-CH_3 stereoselectivity shown by CH_3CCl. The result, however, is the reverse: syn-Cl/syn-CR_3 selectivities for additions to *cis*-butene are 2.84:1 for CH_3CCl[16] and only 1.65:1 for CF_3CCl (Table I).

Among several possible explanations, we prefer the following one. CF_3CCl is a destabilized, highly reactive carbene. Its addition reaction transition states are early and relatively "open", so that differential steric (and electronic) effects are minimized. CH_3CCl, on the other hand, is a more stabilized, less reactive species, which utilizes later, tigher addition transition states, where differential substituent effects are more developed.

Below, we present calculational and experimental evidence supporting this rationalization. Here, however, we note that a similar conclusion emerges from direct comparison of the "steric selectivities" of CF_3CCl and CCl_2. The data of Table II permits calculation of the reactivities of CF_3CCl in additions to RCH=CH_2, relative to 1-butene (R = Et). In Table III, we compare these reactivities to analogous CCl_2 data,[33] with all reactivities measured at 25–30 °C. The CF_3CCl reactivities may also be *partitioned*[34] so as to incorporate the experimental syn/anti preferences (Table I). The resulting partial relative reactivities appear in Table III.

Inspection of the k_{rel} values indicates that CF_3CCl experiences *less* steric retardation than CCl_2 in additions to RCH=CH_2 as a consequence of the increasing size of R, despite the anticipated greater steric demand of CF_3CCl. This conclusion is reinforced by correlating the logarithms of the k_{rel} data with E_s;[30] the correlation slopes (δ) are also shown in Table III. Note that δ_{CF_3CCl} (0.41), which respresents the susceptibility of CF_3CCl to steric hindrance during its addition reactions, is *less* than δ_{CCl_2} (0.88) for CCl_2 additions to the same substrates under comparable conditions. This is so whether we examine δ_{CF_3CCl} on the basis of the overall relative reactivites of CF_3CCl ($\delta = 0.41$) or use the partial relative reactivites ($\delta_{CF_3CCl}^{syn\text{-}Cl} = 0.39$; $\delta_{CF_3CCl}^{syn\text{-}CF_3} = 0.47$). Addition of CF_3CCl to RCH=CH_2 in the syn-CF_3 mode is

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(34) Closs, G. L.; Moss, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 4042.

Table II. Experimentally Observed Relative Reactivities of CF_3CCl (30 °C)

case	olefin a	olefin b	GC condtns: column[a]	GC condtns: T, °C	k_a/k_b[b]
1	*cis*-MeCH=CHMe	$Me_2C=CH_2$	A	60	0.88 ± 0.02
2	*trans*-MeCH=CHMe	*cis*-MeCH=CHMe	A	55	0.71 ± 0.01
3	$Me_2C=CHMe$	$Me_2C=CH_2$	A	70	1.17 ± 0.05
4	$Me_2C=CMe_2$	$Me_2C=CHMe$	A	85	0.72 ± 0.03
5	$Me_2C=CMe_2$	*cis*-MeCH=CHMe	A	65, 95[c]	1.12 ± 0.01
6	*i*-PrCH=CH_2	$EtCH=CH_2$	B	60	0.52 ± 0.02
7	*t*-BuCH=CH_2	*i*-PrCH=CH_2	B	70	0.44 ± 0.02
8	*i*-PrCH=CH_2	$Me_2C=CH_2$	B	60	0.25 ± 0.01

[a] Column A: 19 ft × 0.25 in 15% SF-96 on 80/100 Chromosorb W; injector, 140–150 °C; detector, 170 °C; He flow, 80 mL/min (85 mL/min in case 4). Column B: 20 ft × 3/16 in 10% SE-30 on 80/100 Anakrom ABS; injector, 135 °C; detector, 175 °C; He flow, 60 mL/min (65 mL/min in case 7). [b] Where applicable, relative reactivities were based on composites of syn + anti isomeric cyclopropane products. Errors represent the average deviations of two experiments. [c] Programmed from 65 to 95 °C at 4 °C/min after 18 min at 65 °C.

Table III. Comparative Relative Reactivities of CF_3CCl and CCl_2[a]

substrate (R in RCH=CH_2)	$(k_R/k_{iso})_{CCl_2}$[b]	$(k_R/k_{iso})_{CF_3CCl}$: overall[c]	syn-Cl[d]	syn-CF_3[e]
Et	1.00	1.00	1.12	0.88
i-Pr	0.48	0.52	0.60	0.44
t-Bu	0.051	0.23	0.28	0.17
δ[f]	0.88[g]	0.41	0.39	0.47

[a] $EtCH=CH_2$ is the standard substrate; 25–30 °C. [b] From ref 33. [c] The overall k_{rel} is the sum of both syn-Cl and anti-Cl (=syn-CF_3) additions of CF_3CCl to $RCH=CH_2$. The k_{rel} values are normalized to $EtCH=CH_2$ = 1.00 from the data in Table II. [d] Relative reactivities for addition of CF_3CCl in the syn-Cl mode, calculated from the overall k_{rel} values and the syn-Cl/anti-Cl stereoselectivities of Table I. $k_{rel}^{syn\text{-}Cl}$ values have been multiplied by 2.0 to put them on the same scale as the CCl_2 and overall CF_3CCl k_{rel}'s. [e] Relative reactivities for addition of CF_3CCl in the syn-CF_3 mode; cf. footnote *d*. [f] Slopes of log k_{rel} vs. E_s.[30] [g] From ref 33.

Table IV. Relative Reactivities of XCCl toward Olefins

olefin	X: CF_3[a]	X: CH_3[b]	X: Cl[c]
$Me_2C=CMe_2$	0.92[d]	3.87	8.98
$Me_2C=CHMe$	1.17[e]	2.44[e]	3.12
$Me_2C=CH_2$	1.00	1.00	1.00
cis-MeCH=CHMe	0.88[e]	0.74[e]	0.27
trans-MeCH=CHMe	0.62[f]	0.52	0.18
$EtCH=CH_2$	0.48[e,g]		
i-PrCH=CH_2	0.25[e]		
t-BuCH=CH_2	0.11[e,h]		

[a] This work, 30 °C. [b] Reference 16, 25–30 °C. [c] Reference 36, 25 °C. [d] This is the mean of the reactivities calculated from Table II, cases 4 and 3 ($k_{Me_2C=CMe_2}$ = 0.84) and cases 5 and 1 ($k_{Me_2C=CMe_2}$ = 0.99). The error associated with the mean is estimated to be ±0.08 (~9%). [e] Composite of syn and anti modes of addition to this olefin. [f] Calculated from Table II, cases 2 and 1. [g] Calculated from Table II, cases 6 and 8. [h] Calculated from Table II, cases 7 and 8.

somewhat more sterically demanding than addition in the syn-Cl mode, but *both* δ values are considerably less than δ_{CCl_2}.[35] This point remains valid even if our syn/anti structural assignments (see above) are reversed.

Thus, the larger CF_3CCl behaves as a less sterically demanding carbene than the smaller CCl_2. This is consistent with the idea that CF_3CCl additions proceed through an earlier, more open transition state than the analogous addition reactions of CCl_2.

Discrimination. The CF_3CCl relative reactivites of Table II, adjusted to an isobutene standard (k_{rel} = 1.00), are collected in Table IV, together with analogous results for CH_3CCl[16] and CCl_2.[36] Clearly, CF_3CCl is considerably *less* discriminating across our standard set[15] of olefinic substrates than either CH_3CCl or CCl_2. Notice that CF_3CCl appears to be less reactive toward $Me_2C=CMe_2$[37] than toward $Me_2C=CHMe$, in contrast to the behavior of typical electrophilic carbenes.[15] It might be suggested that this represents a differential steric effect operating against the tetrasubstituted alkene. This is unlikely, however, because CCl_2, which exhibits a *greater* steric demand than CF_3CCl (see above), shows no evidence of steric discrimination against $Me_2C=CMe_2$.

The most generally applicable way to quantitatively measure the olefinic discrimination of an electrophilic carbene is to determine a "carbene selectivity index", m_{CXY}, defined as the least-squares slope of log $(k_i/k_o)_{CXY}$ vs. log $(k_i/k_o)_{CCl_2}$.[15,38] Applied to CH_3CCl, this procedure leads to m_{CH_3CCl} = 0.50, on a scale where m_{CCl_2} = 1.00.[38] The CF_3CCl data cannot readily be treated in this way because of the obvious lack of linearity between the CF_3CCl and CCl_2 (log) k_{rel} data. If the $Me_2C=CMe_2$ substrate is omitted, however, a four-point m_{CF_3CCl} value of 0.19 can be derived from the logarithms of the remaining CF_3CCl and CCl_2 relative reactivities. This correlation is still rather poor, r = 0.91, significant only at the 90% confidence level.

Previously, we showed that the experimentally determined m_{CXY} values of nine carbenes could be correlated by eq 4,[15,38] in which

$$m_{CXY} = -1.10\Sigma_{X,Y}\sigma_R^+ + 0.53\Sigma_{X,Y}\sigma_I - 0.31 \quad (4)$$

$\Sigma_{X,Y}$ represents the sum of the appropriate σ constants[39] for the substituents of CXY. Using[39] $(\sigma_R^+)_{CF_3}$ = +0.08 and $(\sigma_I)_{CF_3}$ = +0.45, together with appropriate σ constants for Cl,[39] we calculate m_{CF_3CCl} = 0.48 from eq 4. This predicts that CF_3CCl should be similar in olefinic selectivity to CH_3CCl (m = 0.50), despite our prejudice that the very different electronic properties of the CF_3[2] and CH_3 substituents should confer rather different olefinic selctivites on their respective chlorocarbene derivatives. If we employ revised[40a] values of $(\sigma_R^+)_{CF_3}$ = +0.20 and $(\sigma_I)_{CF_3}$ = 0.38, we calculate m_{CF_3CCl} = 0.31, significantly less selective than CH_3CCl, but still more selective than the admittedly imprecise experimental value of ~0.19.

(35) Correlations of the k_{rel} data of Table III using DeTar's revised E_s values afford δ's which differ by <3% from the tabulated values obtained with Taft's E_s parameters;[30] cf. DeTar, D. F. *J. Org. Chem.* **1980**, *45*, 5166 and references therein.

(36) See ref 9, p 221.

(37) The relative reactivity ratio for CF_3CCl with $Me_2C=CMe_2$ vs. $Me_2C=CH_2$ could not be determined directly because $Me_2C=CMe_2$ and adduct **4** had similar volatilities and GC behavior. $k_{Me_2C=CMe_2}/k_{Me_2C=CH_2}$ was therefore calculated indirectly in two different ways: cf. Table IV, footnote *d*. Although the estimated error in the final value is ~9%, there is little doubt that $Me_2C=CMe_2$ is not more reactive, and probably somewhat less reactive, toward CF_3CCl than is $Me_2C=CHMe$.

(38) Moss, R. A.; Mallon, C. B.; Ho, C.-T. *J. Am. Chem. Soc.* **1977**, *99*, 4105.

(39) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1.

(40) (a) Private communication from Professor M. Charton, Pratt Institute, Brooklyn, N.Y. These revised σ values are normalized to the Ehrenson et al. scale[39] and are based on the compilation by: Charton, M. *Prog. Phys. Org. Chem.*, in press. We thank Professor Charton for making this information available to us in advance of publication. (b) Weeks, G.; Horák, V. *J. Org. Chem.* **1980**, *45*, 2068.

We also examined an extended form of eq 4 which included a term in σ^- to cope with the strongly electron-withdrawing CF_3 substituent; cf. eq 4a. Equations of this form have been shown

$$m_{CXY} = -1.70\Sigma_{X,Y}\sigma_R^+ + 0.76\Sigma_{X,Y}\sigma_I + 0.64\Sigma_{X,Y}\sigma_R^- - 0.66 \quad (4a)$$

to effectively deal with wide variations of electronic effects.[40b] As before,[38] multiple linear regression analysis of the dependence of m_{CXY}^{obsd} for our nine base carbenes on $(\Sigma_{X,Y})\sigma_I$, σ_R^+, and σ_R^- (A)[39] defined the coefficients of the new correlation equation. Equation 4a correlated the selectivites of the base carbenes better than did eq 4; the standard deviation of differences ($\Delta m = m^{obsd} - m^{calcd}$) was 0.070 for eq 4a vs. 0.089 for eq 4. Similarly, f, the root mean square of the Δm's/root mean square of the experimental m's, was 0.077 for eq 4a vs. 0.092 for eq 4; correlations of acceptable precision have $f < 0.1$.[39] Calculation with eq 4a, using revised[40a] CF_3 values of σ_R^+, σ_I, and σ_R^- (+0.23), gave $m_{CF_3CCl} = 0.25$, in reasonably good agreement with $m_{CF_3CCl}^{obsd} \approx 0.19$.

It is apparent that the olefinic discrimination of CF_3CCl is unusual. The carbene does not display the normal linearity[15] for log k_{rel} vs. log $(k_{rel})_{CCl_2}$, and simulation of its approximate m value requires revision of our correlation equation.[38] However, its observed selectivity is significantly less than that of CH_3CCl, which is both reassuring and intuitively consonant with the expected destabilization of a singlet XCCl by a strongly electron-withdrawing group such as CF_3.[41] On the other hand, CF_3CCl is *not completely unselective*; disregarding the $Me_2C{=}CMe_2$ data in Table IV, we note a clear decrease in CF_3CCl relative addition rates as we progress from tri- to di- to monosubstituted alkenes.

Qualitatively, the expressed selectivity of CF_3CCl places it between HCCOOEt and BrCCOOEt.[38] The latter ($m^{obsd} = 0.29$, $m^{calcd} = 0.26$)[38] is a well-behaved electrophilic carbene, less selective than CH_3CCl ($m^{obsd} = 0.50$, $m^{calcd} = 0.58$),[38] but now seen to be more selective than CF_3CCl ($m^{obsd} \approx 0.19$). On the other hand, HCCOOEt is less selective than CF_3CCl. It too fails to exhibit linearity of k_{rel} vs. $(k_{rel})_{CCl_2}$, but, in addition, it undergoes allylic C—H insertion competitively with addition to C=C,[38] which CF_3CCl does not do.

Again, the data are consistent with a highly reactive, quite unselective, singlet electrophilic CF_3CCl. Recently, we showed that the *absolute* rate constant for addition of PhCCl to $Me_2C{=}CMe_2$ was 1.3×10^8 M^{-1} s^{-1}.[42] Because PhCCl ($m^{obsd} = 0.83$) is considerably *more* discriminating toward alkenes and presumably substantially less reactive than CF_3CCl,[43] it is reasonable to believe that k_{abs} for CF_3CCl addition to $Me_2C{=}CMe_2$ is greater than 1.3×10^8 M^{-1} s^{-1}. Conceivably, the rate of this reaction might approach diffusion control. If so, "k_{rel}" for $Me_2C{=}CMe_2$ could well be out of line with expectations based upon the reactivities of less substituted, less reactive alkenes. Alternatively, the compensation between differential enthalpies and entropies of activation, upon which the observed relationships[15] between carbene/alkene structure and reactivity probably rest,[45] may well fail for carbenes as reactive as CF_3CCl or HCCOOEt.

Additional support for the experimental picture of a highly reactive, quite unselective CF_3CCl emerges from ab initio calculations. The geometry and orbital energies (HOMO and LUMO) of CF_3CCl were calculated by STO-3G/4-31G procedures.[46] The C—C and C—Cl bond lengths and the CCCl angle of CF_3CCl were optimized by using the STO-3G basis set; the CF_3 geometry was fixed by using standard values. Next, the frontier molecular orbital energies were calculated by using the 4-31G basis set. The 4-31G orbital energies of the singlet carbene were found to be −0.33 eV (LUMO or p) and −11.96 eV (HOMO or σ). Next, we calculated the *carbene stabilization energy*, ΔE_{stab}^{CXY}, the stabilization of CXY relative to the corresponding substituted methane according to the isodesmic reaction (5). The

$$CH_2 + CH_3X + CH_3Y \xrightarrow{-\Delta E_{stab}} CXY + 2CH_4 \quad (5)$$

negative of the 4-31G energy of eq 5 is defined as ΔE_{stab}^{CXY}.[46] The ΔE_{stab} of CF_3CCl was found to be 1.40 kcal/mol, a much lower stabilization energy than those of 12 previously studied carbenes.[44] ΔE_{stab} of CH_3CCl, for example, was calculated as 29.3 kcal/mol. Obviously, the exchange of CF_3 (CF_3CCl) for CH_3 (CH_3CCl) greatly destabilizes the carbene.

There is a direct relation between ΔE_{stab} and carbenic selectivity. Indeed, ΔE_{stab} and m_{CXY} afford linear correlation 6.[44] The very

$$m_{CXY}^{calcd} = 0.035\Delta E_{stab} - 0.449 \quad (6)$$

low calculated ΔE_{stab} for CF_3CCl thus indicates a very unselective carbene. There are some problems with the calculations, however. The calculated C—C bond length (1.630 Å) is obviously too long, and we suspect that ΔE_{stab} is too low. Indeed, correlation 6 predicts $m_{CF_3CCl} = -0.4$ (based on $\Delta E_{stab} = 1.40$), an impossible value. Put the other way, taking $m_{CF_3CCl}^{obsd} \approx 0.19$, the $\Delta E_{stab}/m_{CXY}$ correlation gives $\Delta E_{stab}^{CF_3CCl} \approx 18$ kcal/mol. Although much larger than the 4-31G ΔE_{stab} for CF_3CCl, this value is 11 kcal/mol *less* than ΔE_{stab} calculated for CH_3CCl and still corresponds to significant carbenic destabilization due to the CF_3 substituent.

In summary, all experimental results, as well as a brief theoretical study, describe CF_3CCl as a highly reactive, unselective carbene which adds to alkenes via early, relatively open transition states. This behavior reflects the destabilizing character of the strongly electron-withdrawing CF_3 substituent.[2,41] Despite its low selectivity, CF_3CCl adds stereospecifically to the 2-butenes and, with simple alkenes, does not insert into allylic C—H bonds competitively with C=C addition. CF_3CCl is the most unselective carbene for which an m value has been even approximately defined, and its reactions should serve as a good model for those of other poorly stabilized (or destabilized), singlet, disubstituted carbenes.

Experimental Section

General Data. Proton NMR spectra were normally recorded with a Varian T-60 spectrometer; chemical shifts are reported in δ units. Fluorine NMR spectra were normally recorded with a Varian FT-80 spectrometer (broad-band probe); chemical shifts are reported in parts per million upfield from an internal CCl_3F reference. Gas chromatography employed Varian Aerograph Model 90P and 1700 instruments. Mass spectra were determined with a Hewlett-Packard Model 5985 GC–MS system. Microanalyses were performed by Robertson Laboratory, Florham Park, N.J.

3-Chloro-3-(trifluoromethyl)diazirine (1).[13,17] Anhydrous ammonia (50 g) was condensed into a 100-mL three-neck flask, equipped with a magnetic stirring bar and cooled in a Dry-Ice/acetone bath. To this stirred solution was added 10 g (105 mmol) of trifluoroacetonitrile (Columbia Organics) slowly via a gas inlet tube over 2.5 h at −60 to −70 °C. After addition, the solution was refluxed (Dry-Ice/acetone condenser) for 30 min. Excess ammonia was removed by evaporation at 20 °C, and residual ammonia was removed by three freeze/pump/thaw cycles (−30 °C (<1mmHg)). The product, trifluoroacetamidine, was obtained in about 90% yield and was generally used without further purification. Alternatively, the crude product could be fractionated under reduced pressure (bp 34–35 °C (11mmHg) (lit.[47] bp 35–36 °C (11mmHg)).

Oxidation was carried out by Graham's procedure.[13,18] To a cooled (0 °C) solution of 6.72 g (60 mmol) of trifluoroacetamidine and 11.6 g of LiCl in 200 mL of Me_2SO was quickly added 500 mL of aqueous sodium hypochlorite solution,[48] saturated with NaCl. The reaction solution was rapidly stirred during addition and continuously evacuated (P < 1mmHg) through a train composed of a U-tube filled with NaOH

(41) For examples and leading references to destabilzing effects of the CF_3 group, see: Greenberg, A.; Liebman, J. F.; Van Vechten, D. *Tetrahedron* **1980**, *36*, 1161.

(42) Turro, N. J.; Butcher, J. A., Jr.; Moss, R. A.; Guo, W.; Munjal, R. C.; Fedorynski, M. *J. Am. Chem. Soc.* **1980**, *102*, 7576.

(43) Carbene–alkene addition reactions appear to follow the reactivity-selectivity principle.[44]

(44) Rondan, N. G.; Houk, K. N.; Moss, R. A. *J. Am. Chem. Soc.* **1980**, *103*, 1770.

(45) Skell, P. S.; Cholod, M. S. *J. Am. Chem. Soc.* **1969**, *91*, 7131.

(46) Details and leading references for these procedures may be found in ref 44.

(47) Reilly, W. L.; Brown, H. C. *J. Am. Chem. Soc.* **1956**, *78*, 6032.

(48) Commercial liquid "pool chlorine", 12.4% sodium hypochlorite by weight, was used.

pellets, followed by three traps. The first trap was cooled to −77 °C, while the second and third traps were cooled to 77 K with liquid nitrogen. The last trap contained 1 mL of pentane. Diazirine **1** which collected in the second trap was cautiously distilled under vacuum at 25 °C into the third trap. The final pentane solution of **1** was used without further purification. The yield was ~45%, and the spectral characterization of **1** has been reported.[13,49] *Caution*: Diazirine **1** is potentially explosive.

Synthesis of Cyclopropanes. General Procedure. About 15 mL of the desired alkene was added (or condensed) into a screw-top (Pyrex) Carius tube, which also contained a small magnetic stirring bar. The alkene was cooled to −78 °C, and the pentane/diazirine solution was added. The tube was sealed and warmed to 25 °C, and the contents were stirred and photolyzed for 3 h at 25–30 °C by using a focused Osram 200-W Xe mercury lamp. After photolysis, the reaction solution was cooled to −78 °C, the tube was opened, and the alkene was cautiously evaporated by warming. Crude products were then subjected to GC for product isolation and analysis. Yields of GC-isolated cyclopropanes ranged from 2 to 12% on the basis of (trifluoromethyl)acetamidine (~4 to 27% on the basis of diazirine **1**).

1-Chloro-1-(trifluoromethyl)-2,2,3,3-tetramethylcyclopropane (2).[12] This product was formed from CF_3CCl and $Me_2C{=}CMe_2$ and was isolated by GC on an 11 ft × 0.25 in. 15% SF-96 on 80/100 Chromosorb W column at 85 °C (injector, 135 °C; detector, 170 °C; He flow, 60 mL/min). The retention time was 15.3 min. The proton NMR spectrum (δ, CCl_4) showed overlapping singlets at 1.25 (lit.,[12] 1.23). Mass spectrum: m/e 200, 202, M^+; base peak, $M^+ - Cl$.

1-Chloro-1-(trifluoromethyl)-2,2,3-trimethylcyclopropanes (3-*syn*-Cl and 3-*anti*-Cl).[12] These products were formed from CF_3CCl and trimethylethylene. They were isolated as a mixture by GC, using the column described for **2**, at 80 °C (injector, 150 °C; detector, 170 °C; He flow, 60 mL/min): retention times, 18.1 and 19.2 min; NMR (δ, CCl_4) 0.95–1.50 (m) (lit.,[12] 0.97–1.57); ^{19}F NMR ($CDCl_3$, $CFCl_3$) major isomer, 63.9, minor isomer, 59.8;[20] ratio, 1.48:1. Mass spectrum, m/e 186, 188, M^+, base peak, $M^+ - Cl$.

1-Chloro-1-(trifluoromethyl)-2,2-dimethylcyclopropane (4). This product was formed from isobutene and CF_3CCl. It was isolated on column A (Table II) at 70 °C (injector, 150 °C; detector, 170 °C; He flow, 60 mL/min): retention time, 14.3 min; proton NMR (δ, CCl_4) 1.0 (m, 1 H, cyclopropyl H), 1.37, 1.43 (2"s" + m, 7 H, CH_3's + cyclopropyl H); mass spectrum, m/e 172, 174, M^+, base peak, $M^+ - Cl$.

1-Chloro-1-(trifluoromethyl)-*cis*-2,3-dimethylcyclopropanes (5-*syn*-Cl and 5-*anti*-Cl).[12] These products were formed from CF_3CCl and *cis*-butene and were isolated by GC on column A (Table II) at 70 °C (conditions as for **4**). The major isomer eluted first (15.7 min), followed by the minor isomer (18 min). The 60-MHz NMR spectrum of **5-syn-Cl** (major) showed (δ, CCl_4) 1.10 ("d", CH_3's) and 1.23–1.77 (m, cyclopropyl). The minor isomer (**5**-anti-Cl) showed 1.27 ("d", CH_3's) and 1.50–1.93 (m, cyclopropyls). The GC isomer ratio was 1.65:1. Detailed discussions of the ^1H and ^{19}F NMR appear in the Results. Mass spectrum (each isomer): (m/e) 172, 174, M^+.

1-Chloro-1-(trifluoromethyl)-*trans*-2,3-dimethylcyclopropane (6).[12] This product was formed from CF_3CCl and *trans*-butene and was isolated by GC on the column used for **2** at 60 °C (injector, 135 °C; detector, 170 °C, He flow, 60 mL/min): retention time, 10.1 min; NMR (δ, CCl_4) 1.17 (b s, CH_3's) and 1.70–1.57 (m, cyclopropyl H's) (lit.,[12] 1.11, 0.97–1.44); mass spectrum, m/e, 172, 174, M^+; base peak, $M^+ - Cl$.

1-Chloro-1-(trifluoromethyl)-2-ethylcyclopropanes (7-*syn*-Cl and 7-*anti*-Cl). These isomers were formed from CF_3CCl and 1-butene and were separated on column B (Table II) at 60 °C (injector, 125 °C; detector, 175 °C; He flow, 50 mL/min): retention times, 10 min, 50 s (major) and 12 min, 12 s (minor); GC isomer ratio, 1.28; ^1H NMR (isomer mixture, δ, CCl_4, CH_2Cl_2) 0.73–1.80; ^{19}F NMR ($CDCl_3$, $CFCl_3$) 72.82 (major), 65.85 (minor).[20] Anal. C, H, Cl.

1-Chloro-1-(trifluoromethyl)-2-isopropylcyclopropanes (8-*syn*-Cl and 8-*anti*-Cl). These isomers were formed from CF_3CCl and isopropylethylene and were separated on column B (Table II) at 60 °C, using the conditions described for **7**: retention times, 22 min (major) and 23 min, 30 s (minor); GC isomer ratio, 1.36; ^1H NMR (isomer mixture, δ, CCl_4, CH_2Cl_2) 1.0 ("d", J = 5 Hz, *i*-Pr methyls), 1.13–1.60 (m, cyclopropyl + carbinyl H's); ^{19}F NMR ($CDCl_3$, $CFCl_3$) 74.75 (major), 67.59 (minor).[20] Anal. C, H, Cl.

1-Chloro-1-(trifluoromethyl)-2-*tert*-butylcyclopropanes (9-*syn*-Cl and 9-*anti*-Cl). These isomers were formed from CF_3CCl and *tert*-butylethylene and were separated on column B (Table II) at 85 °C (injector, 125 °C; detector, 175 °C; He flow, 65 mL/min): retention times, 11 min, 49 s (major) and 12 min, 56 s (minor); GC isomer ratio, 1.66; ^1H NMR (δ, CCl_4, mixture of isomers) 1.07, 1.12 (singlets, 9 H, *t*-Bu's of minor and major adducts, respectively), 1.23–1.73 (m, 3 H, cyclopropyl H's); ^{19}F NMR ($CDCl_3$, $CFCl_3$) 75.4 (major), 65.4 (minor).[20] Anal. C, H, Cl.

Competition Experiments. These were run on carefully weighed binary mixtures of olefins, using diazirine **1** prepared from 20 mmol of trifluoroacetamidine (see above). Details of procedure and analysis appear in the Results. See Table II for tabulated results and analytical conditions.

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(49) We observed UV maxima for **1** at 333 and 318 nm (pentane, −63 °C) (lit.,[13] λ_{max} = 318 (gas phase)).

(50) Both **5-*syn*-Cl** and **5-*anti*-Cl** were subjected to heteronuclear decoupling NMR experiments in which their methyl protons were irradiated and their CF_3 resonances were observed. Significant nuclear Overhauser effects were observed in neither compound.