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Laser Flash Photolysis Study of Chlorofluorocarbene

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10-*exo*-Fluoro-10′-endo-chlorotricylco[4.3.1.0^{1,6}]decadiene-2,4 (**1**) was synthesized. Continuous photolysis of **1** (300 nm) generates chlorofluorocarbene **2**, which can be intercepted with tetramethylethylene (TME) to form the expected cyclopropane **3**. Laser flash photolysis (LFP) of **1** (308 nm) in cyclohexane at ambient temperature does not result in the direct detection of **2** by time-resolved UV−vis spectroscopy. However, LFP of **1** in the presence of pyridine produces the intense transient absorption of ylide **4** at 450 nm. The absolute rate constant of reaction of **2** with pyridine is 8.0×10^9 M^{-1} s^{-1} in cyclohexane. LFP (266 nm) of **1** in heptane at ambient temperature produces a transient species with a C−F vibration at 1142 cm^{-1} and a lifetime of 2.5 μs at ambient temperature. The carrier of the transient absorption is assigned to carbene **2** on the basis of density functional theory (DFT) calculations and on the basis of its kinetic behavior. The absolute rate constant of reaction of carbene **2** with TME was determined by monitoring the transient absorption of ylide **4** (Freon-113) or by time-resolved IR spectroscopy (heptane) to give values of 1.1×10^8 M^{-1} s^{-1} and 2.9×10^8 M^{-1} s^{-1}, respectively. This is the first measurement of a bimolecular ground-state singlet carbene reaction by both time-resolved UV−vis and IR spectroscopy. The value determined by the time-resolved IR measurement is more accurate than that from the ylide probe technique.

I. Introduction

Laser flash photolysis (LFP) studies of triatomic chlorocarbenes have been reported. The absolute reactivities of chloro[1] and dichlorocarbene[2] were measured using the pyridine ylide probe method. In this study, we report analogous studies of a mixed dihalocarbene, CFCl, and demonstrate the utility of time-resolved infrared (TRIR) spectroscopy for the direct observation of fluorinated carbenes.[3]

II. Experimental Section

General Methods. ^{1}H NMR spectra were obtained on a Bruker DRX-250 (250 MHz) or DRX-400 (400 MHz) spectrometer. The GC-MS spectrometer was an HP-6890 series GC system with an HP-1 methyl siloxane capillary column (40.0 m × 100 μm × 0.20 μm). The gas chromatograph was linked to an HP 5973 mass-selective detector.

Tetrahydrofuran was purified by distillation from sodium benzophenone under argon. Benzene, heptane (HPLC grade), and cyclohexane were distilled from calcium hydride under argon. Freon-113 (Aldrich Chemical Co.) was distilled under argon from P_2O_5 using a 40-cm distillation column.

Laser Flash Photolysis Studies.[4] For LFP studies of precursor **1**, a stock solution was prepared in Freon-113. Samples (1 mL) were prepared with an optical density of 0.1 at 308 nm. The LFP apparatus utilized a Lambda Physik LPX-100 excimer laser (308 nm, 120 mL, 10 ns). The analysis of data was performed using the Igor Pro software package from Wavemetrics. Transient absorption spectra were obtained on an EG&G PARC 1460 optical mutichannel analyzer fitted with an EG&G PARC 1304 pulse amplifier, an EG&G PARC 1024 UV detector, and a Jarrell-Ash 1234 grating.

Matrix Isolation Spectroscopy. The precursor was placed in a glass U tube that was connected directly to a helium closed-cycle cryostat (Air Products). Argon gas streaming over the precursor was condensed on the surface of a CsI window held at ca. 18 K. The IR spectra were recorded on a Perkin-Elmer FT-IR 2000 interferometer at 0.2 cm^{-1}. A Ray-O-Net reactor was used to photolyze the sample.

Crystallography. See Table S1 of the Supporting Information.

Time-Resolved Infrared (TRIR) Studies. TRIR experiments were conducted with a JASCO TRIR-1000 dispersive-type IR spectrometer with 16-cm^{-1} resolution following the method described in the literature.[5−7] Briefly, a reservoir of the deoxygenated sample solution (10 mL of 5 mM **1)** was continuously circulated between two barium fluoride salt plates with a 0.5-mm path length. The sample was excited by 266-nm laser pulses of a Nd:YAG laser (40 Hz repetition rate, 0.5−0.7 mJ/pulse power), which is crossed with the broadband output of a $MoSi_2$ IR source (JASCO). The intensity change of the IR light induced by photoexcitation is monitored as a function of time by an MCT photovoltaic IR detector (Kolmar Technologies, KMPV11-1-J1) with a 50-ns rise time, amplified with a low-noise NF Electronic Instruments 5307 differential amplifier and digitized with a Tektronix TDS784D oscilloscope. The TRIR spectrum is analyzed by the IGOR PRO program (Wavemetrics Inc.) in the form of a difference spectrum:

$$\Delta A_t = -\log(1 + \Delta I_t/I)$$

where ΔI_t is the intensity change induced by photoreaction at time t and I is the IR intensity for the sample without photoexcitation. Thus, the depletion of reactant and the formation of transient intermediates or products lead to negative and positive signals, respectively.

Density Functional Calculations. Geometries of singlet **2**, precursor **1**, triene **5**, and biradical **6** were fully optimized at the B3LYP level of theory with the 6-31G* basis set; harmonic

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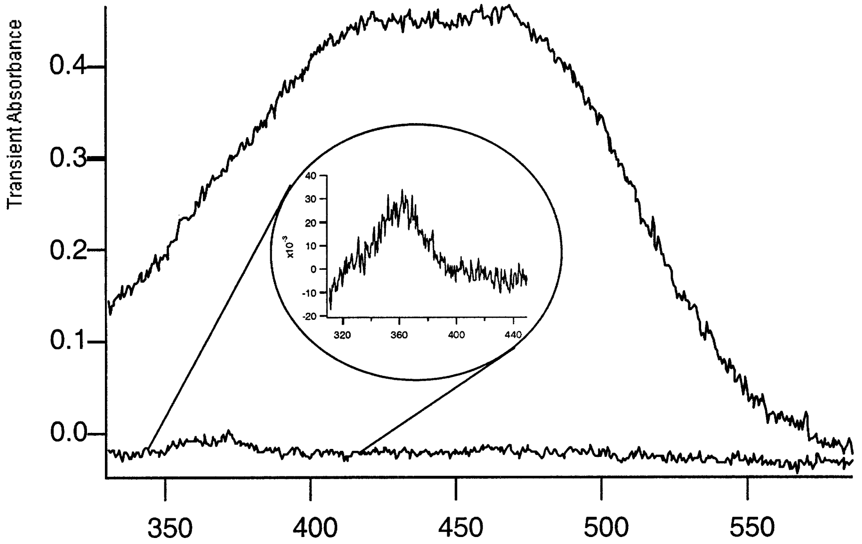


Figure 1. Transient spectra produced by LFP of **1** in Freon-113 at ambient temperature in the presence of (top, 1 M) and absence of (bottom) pyridine. The spectra were recorded 20 ns after the laser pulse over a window of 20 ns.

frequencies and UV−vis spectra (for **1** and **5**) were calculated at the same level of theory. All calculations were carried out with the Gaussian 98 program package.[8] Vibrational frequencies were scaled by a factor of 0.9613.

Synthesis. *10-exo-Fluoro-10-chlorotricyclo[4.3.1.0^{1,6}]decadiene-2,4* (**1**). To a stirred solution of 10,10′-dichlorotricylco[4.3.1.0^{1,6}]-decadiene-2,4[9] (1.69 g, 8.4 mmol) in 70 mL of THF maintained at −78° C 1.1 eq of n-BuLi was added dropwise. After 1 h, a solution of *N*-fluorobenzenesulfonamide (2.92 g, 9.2 mmol) in 20 mL of THF was added dropwise to the reaction with stirring. The reaction was allowed to warm gradually to ambient temperature and was poured into water (100 mL) and extracted with diethyl ether (3 × 75 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation to yield a crude red oil. The oil was passed over silica gel (hexane elution) to yield a white crystalline compound in 85% yield. ^1H NMR (250 MHz, $CDCl_3$, δ): 1.6−1.9 (m, 2H), 1.98−2.1 (m, 2H), 2.42−2.55 (m, 2H), 5.87 (dd, 2H, J = 7.6 Hz), 6.08 (dd, 2H, 7.3 Hz). ^{13}C (126 MHz, $CDCl_3$, δ): 25.7 (d, J_{CF} = 8.6 Hz), 33.9 (d, J_{CF} = 4.4 Hz), 49.9 (d, J_{CF} = 14.5 Hz), 96.6 (d, J_{CF} =290.6 Hz), 121.9, 123.1 (d, J_{CF} = 2.7 Hz). ^{19}F NMR (235 MHz, $CDCl_3$, δ): −164.97 (s).

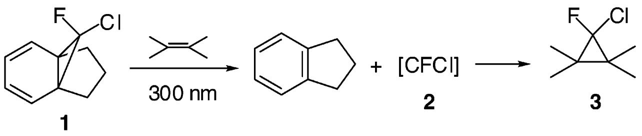
Adduct 3. *Photochemical Preparation.* Compound **1** (73 mg) as a stirred solution in 2,3-dimethyl-2-butene (5 mL) was irradiated with 300-nm light (Ray-O-Net reactor) for 13 h. Indan and adduct peaks were identified by comparison with authentic materials. Yields were determined from GC/MS analysis using adamantane as an internal standard. The mixture was concentrated by rotary evaporation at 20 °C, filtered through silica with hexanes as the eluant, and analyzed by ^1H NMR spectroscopy. ^1H NMR (250 MHz, $CDCl_3$, δ): 1.13 (d, J = 2.1 Hz, 6H), 1.14 (d, J = 1.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 15.9 (d, J_{CF} = 9.1 Hz), 19.2, 27.7 (d, J_{CF} = 9.8 Hz), 105 (d, J_{CF} = 290 Hz). ^{19}F NMR (235 MHz, $CDCl_3$, δ): −147.15. MS (EI) *m/z* (relative intensity): 150 (5%), 135 (100%).

Adduct 3. *Chemical Preparation.* Adduct **3** was prepared according to a literature procedure.[10] ^1H NMR (250 MHz, $CDCl_3$, δ): 1.13 (d, J = 2.1 Hz, 6H), 1.14 (d, J = 1.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 15.88 (d, J_{CF} = 9.1 Hz), 19.2, 27.7 (d, J_{CF} = 9.8 Hz), 105 (d, J_{CF} = 290 Hz). ^{19}F NMR (235 MHz, $CDCl_3$, δ): −146.41.

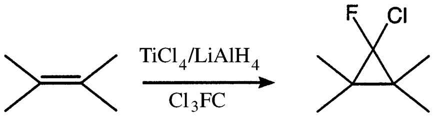
III. Results

Jones' dichloride[9] was treated with butyllithium and *N*-fluorobenzenesulfonamide to afford **1** as a highly crystalline compound in good yield, and its structure was proven by X-ray crystallography. (See Supporting Information Figure S1.)

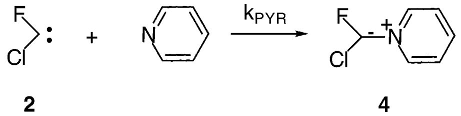
Continuous photolysis (300 nm) of **1** in neat tetramethylethylene (TME) provides evidence for the formation of carbene **2** in solution because indan and cyclopropane **3** are formed in 97 and 77% yield, respectively.



The structure of **3** was confirmed by an independent synthesis of this known compound.[10]



Laser Flash Photolysis. Laser flash photolysis (LFP, 308 nm) of **1** in cyclohexane at ambient temperature produces the transient spectra of Figure 1 in the presence (top) and absence (bottom) of pyridine. Indan does not absorb significantly above 300 nm and was not detected by this technique. The broad, intense band absorbing at 450 nm detected in the presence of pyridine is attributed to ylide **4**, formed by trapping carbene **2**.



The absorption maximum of **4** is similar to that observed with CCl_2 (390 nm).[2] Further support of this assignment is provided by the fact that the pseudo-first-order rate constant of formation (k_{obs}) of the species absorbing at 450 nm is linearly dependent on the concentration of pyridine (Figure 2). The absolute rate constant of reaction of carbene **2** with pyridine is the slope of this plot ($k_{pyr} = 8.0 \times 10^9$ M^{-1} s^{-1}); the carbene lifetime in the

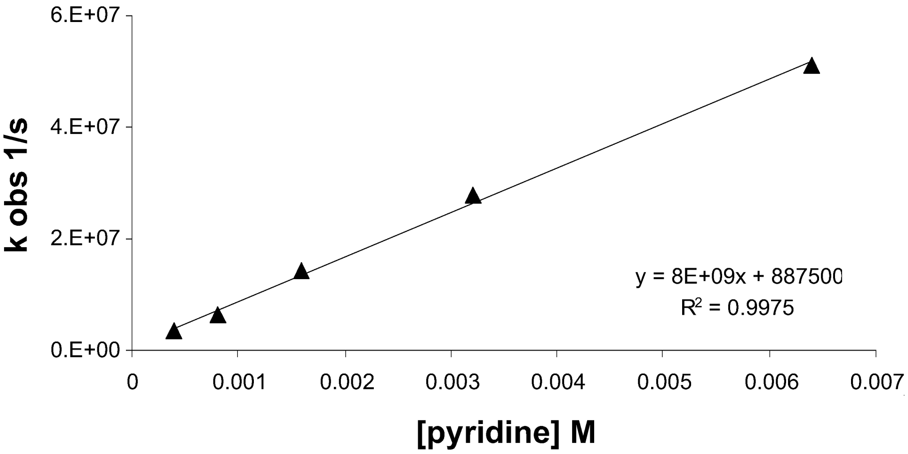


Figure 2. Plot of k_{obs} of formation of ylide **4** versus pyridine concentration in cyclohexane at ambient temperature.

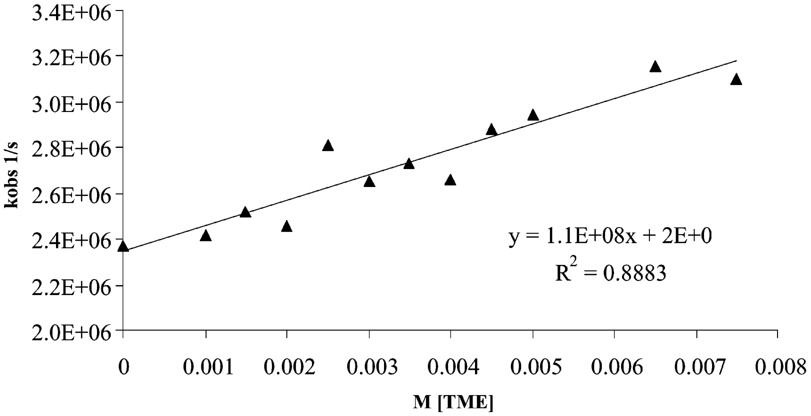


Figure 3. Plot of k_{obs} of formation of ylide **4** at constant pyridine concentration (0.002 M) as a function of [TME] in Freon-113 at ambient temperature.

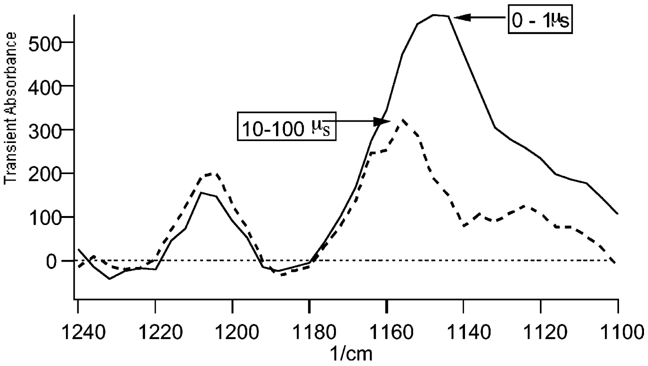


Figure 4. TRIR sprectrum produced by LFP (266 nm) of **1** in heptane at ambient temperature (1 μs/div).

absence of pyridine is 1.1 μs. These results are similar to those reported for dichlorocarbene.[2]

The rate of formation of ylide **4** is accelerated by the addition of tetramethylethylene (TME) at constant pyridine concentration (0.002 M). An analysis of the data reveals that the absolute rate constant of reaction of carbene **2** with TME is 1.1×10^8 M^{-1} s^{-1} in Freon-113 (Figure 3).

Time-Resolved Infrared Spectroscopy. LFP (266 nm) of **1** in heptane produces the transient IR difference spectrum of Figure 4. The negative peak observed at 1180 cm^{-1} is due to the consumption of precursor **1**. The carrier of the positive TRIR peak observed at 1142 cm^{-1} has a lifetime of 2.5 μs. The decay of transient absorption at 1142 cm^{-1} is linearly dependent on the concentrations of TME ($k_{TME} = 3 \times 10^8$ M^{-1} s^{-1}, heptane, Figure 5) and either LiBr or $ZnBr_2$ ($k_{LiBr} = 5.3 \times 10^8$ M^{-1} s^{-1}; $k_{ZnBr2} = 2.1 \times 10^8$ M^{-1} s^{-1}, acetonitrile, see Supporting Information Figures S2 and S3). The products expected in the metal salt reactions are carbenoids.[11,12] The carbenoid reaction products were not observed by TRIR spectroscopy. The carbene lifetime and k_{TME} values obtained by TRIR spectroscopy are similar to those obtained by LFP with UV−vis detection; thus the carrier of transient absorption at 1142 cm^{-1} is attributed to carbene **2**.

At later times (>10 μs after the laser flash), a peak at 1160 cm^{-1} also appears and is assigned to the C−F stretch of the product of carbene reaction with solvent. In all solvents studied (benzene, acetonitrile, cyclohexane, and heptane), photolysis of **1** generates a peak at 1210 cm^{-1}. The growth of this peak is faster than the time resolution of our instrument (<200 ns), and its decay exceeds the limit of our instrument (~1 ms). The peak is unchanged in either its intensity or its kinetics in the presence of LiBr, TME, or oxygen. The carrier of this band will later be attributed to triene **5**.

Matrix Isolation. Chlorofluorocarbene has been previously isolated in a low-temperature matrix.[13] The reported carbene C−F vibration was reported by Smith et al. at 1146 cm^{-1}. We were able to deposit independent precursor **1** in an argon matrix at 18 K. Photolysis (254 nm) bleaches the IR bands of precursor **1**. We simultaneously observe the production of three photoproduct peaks assignable to a C−F vibration at 1210, 1160, and 1115 cm^{-1} (Figure 6).

IV. Discussion

Computational Chemistry. Density functional theory (DFT) calculations with the 6-31G* basis set were performed to

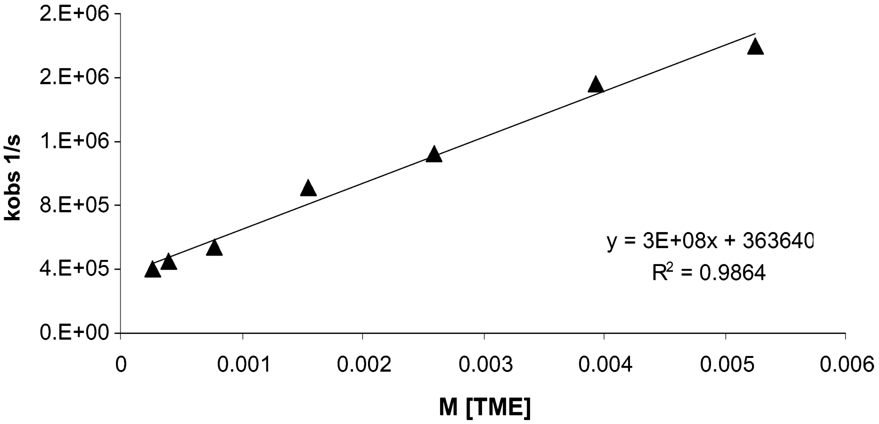


Figure 5. Plot of k_{obs} of the decay of the transient absorbing at 1142 cm^{-1} as a function of [TME] in heptane at ambient temperature.

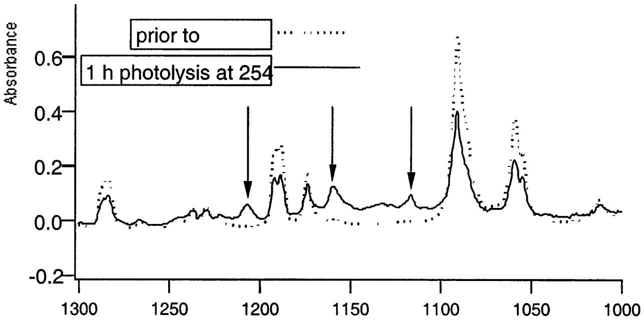


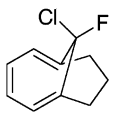
Figure 6. Argon matrix photolysis (254 nm) of **1** at 18 K. Arrows mark the photoproduct peaks (cm^{-1}).

TABLE 1: Calculated and Experimental ν_{C-F} Frequencies

compound	experiment (cm^{-1})	theory (cm^{-1})^{c}
1	$1180^{a,b}$	1073
2	$1142^{a,}1160^{b}$	1169
5	$1210^{a,b}$	1058
6	1115^{b}	1019

[a] TRIR. [b] Argon matrix. [c] B3LYP calculations with the 6-31G* basis set after scaling by a factor of 0.9613.

validate the IR spectroscopic assignments.[8] Minimum-energy geometries (Supporting Information) of diene **1**, carbene **2**, triene **5**, and triplet biradical **6** were calculated and are given in the Supporting Information section. The C−F vibrational frequencies of the compounds of interest, after scaling by a factor of 0.9613, are given in Table 1. The calculations are in fair to poor agreement with our assignments of the experimental data. Other groups have noted this level of modest agreement of theory and experiment before with related fluoro compounds.[14]



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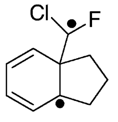

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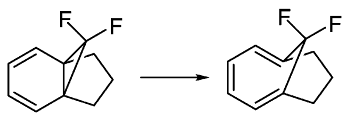
Diene **7** spontaneously isomerizes to triene **8**.[15] The presence of two strongly electronegative substituents on a cyclopropyl ring is known to cause considerable increases in ring strain.[15−17]



7 **8**

TABLE 2: Calculated (TD-DFT) Absorption Spectra of Diene 1 and Triene 5

compound	absorption maxima (nm)	*f*
1	277	0.0501
4	389	0.2238
5	285	0.007

The UV−vis spectra of diene **1** ($\epsilon_{270} = 3663$ M^{-1} cm^{-1}) and triene **8** ($\epsilon_{268} = 4242$ M^{-1} cm^{-1}; Supporting Information, Figure S4) were recorded. It is clear that the triene absorbs at longer wavelength than a related diene. This is confirmed by TD-DFT calculations of **1** and **5** (Table 2). Thus, it seems likely that the long-lived species formed by flash photolysis of **1** and detected at 360 nm and 1210 cm^{-1} is triene **5**. The 1210-cm^{-1} band observed in argon at 18 K is also assigned to **5**. Photolysis of **1** must lead to some isomerization to produce triene **5** in addition to some fragmentation to form carbene **2**. This partitioning can occur via the intermediacy of biradical **6**.

A vibrational band was observed at 1210 cm^{-1} upon photolysis of diene precursor **1** in both the argon matrix and liquid-phase TRIR experiments. Thus, the carrier of this vibrational band cannot be due to the reaction of carbene or another species with solvent. The lack of reactivity of the carrier of this spectral band with oxygen, a radical quencher, excludes biradical **6** as the carrier of the 1210-cm^{-1} transient absorption. These observations are consistent with our previous attribution of the carrier of this band to triene **5**, despite the fact that this assignment is in poor agreement with DFT calculations.

A very similar reactivity pattern is seen in the case of 10-exo-carbomethoxy-10-fluorotricyclo[4.3.1.0^{1,6}]decadiene 2,4,5. In this system, a new long-lived IR band is produced upon photolysis of a tricyclic precursor that is blue shifted from the region of precursor bleaching.[17]

At this time, we cannot confidently assign the carrier of the 1115-cm^{-1} band in argon. It is certainly not indan, whose vibrational spectrum is known.[18] (See also Supporting Information.) It is conceivable that the carrier of the 1115-cm^{-1} band in argon is triplet biradical **6**, which is predicted to have its C−F stretch at 1019 cm^{-1} after scaling by a factor of 0.9613.

The TRIR spectrum shown in Figure 4 contains two peaks that persist 10 μs after laser flash photolysis of the precursor. The growth of the peak at 1160 cm^{-1} is probably due to a C−H insertion reaction of carbene with solvent to form a stable product. This band is masked by its proximity to the bleaching of the precursor (1180 cm^{-1}) and the growth and decay of the carbene (1142 cm^{-1}).

Chlorofluorocarbene is found to have bimolecular reactivity similar to that of chloro and dichlorocarbene.[2] These three carbenes react with pyridine with near diffusion-controlled rates. Chlorofluorocarbene reacts with tetramethylethylene with rate constants on the order of 10^8 M^{-1} s^{-1}, which is about 10 times slower than the corresponding reaction of dichlorocarbene with this alkene.[2] CFCl has a lifetime of microseconds in heptane. This lifetime value is comparable to that of CCl_2 but is much longer than that of chlorocarbene.[1]

V. Conclusions

Mixed dihalocarbene CFCl is produced upon photolysis of **1**. In continuous photolysis experiments, the carbene is trapped with tetramethylethylene (TME) to form the anticipated cyclopropane. In laser flash photolysis experiments, CFCl can be trapped with pyridine to form an ylide ($k_{pyr} = 8 \times 10^9$ M^{-1} s^{-1}, $\tau = 1.1$ μs). The absolute rate constant of reaction of CFCl with TME was found to be ($k_{TME} = 1.1 \times 10^8$ M^{-1} s^{-1}) using the pyridine ylide probe technique in Freon-113. LFP of **1** with IR detection produces CFCl with $\nu_{C-F} = 1142$ cm^{-1} and $\tau =$ 1−3 μs. The value of k_{TME} determined by time-resolved infrared spectroscopy is 2.9×10^8 M^{-1} s^{-1} in heptane and is in fair agreement with the value determined by LFP in Freon-113. The spectroscopic assignments are in fair to poor agreement with density functional theory calculations.

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Supporting Information Available: The X-ray crystal structure of **1** and an ORTEP drawing of **1** are provided. The experimental and calculated IR spectra of indan are provided. A plot of k_{obs} versus [LiBr] and [$ZnBr_2$] is provided along with the UV−vis spectra of **1** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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