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► **To cite this version:**

B. Noller, L. Poisson, R. Maksimenka, I. Fischer, J.-M. Mestdagh. Femtosecond Dynamics of Isolated Phenylcarbenes. *Journal of the American Chemical Society*, 2008, 130 (45), pp.14908-14909. 10.1021/ja804133c . hal-00341195

**HAL Id: hal-00341195**

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Submitted on 24 Nov 2008

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## Supporting Information (6 pages)

### ***Femtosecond Dynamics of isolated Arylcarbenes***

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#### **a) Experimental Details**

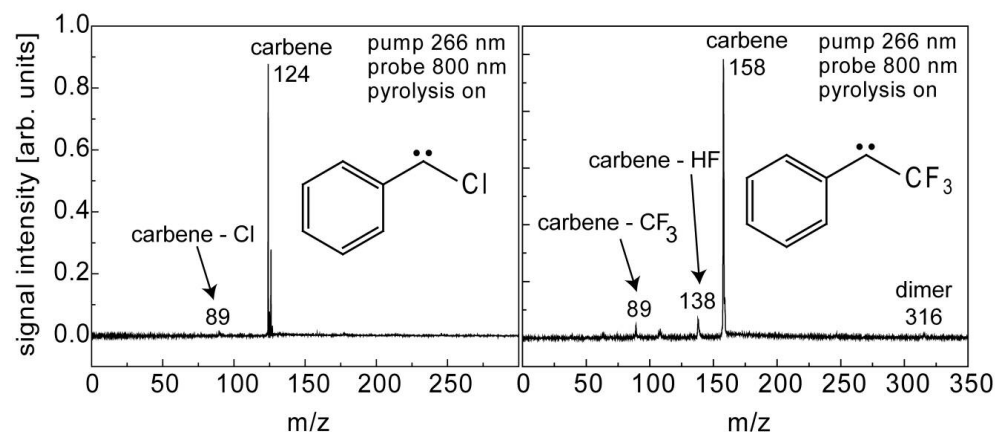
The experiments were performed in a standard molecular beam apparatus. A cold beam of arylcarbenes was prepared by supersonic jet flash pyrolysis<sup>1</sup> of diazirines (3-phenyl-3-(trifluoromethyl)diazirine (TFPC) and 3-phenyl-3-chlorodiazirine (CPC)), synthesized according to the literature.<sup>2,3</sup> The precursor was seeded in 3 bars of argon and expanded through a short, weakly heated SiC tube attached to a water cooled solenoid pulsed valve operating at 20 Hz. The pressure of the source chamber lay at  $2 \times 10^{-5}$  mbar. After passing a 1-mm skimmer, the molecular beam reached the detection chamber ( $2 \times 10^{-7}$  mbar), which was equipped with a time-of-flight mass spectrometer (TOF-MS) and a velocity map imaging (VMI) spectrometer used for mapping ion or electron kinetic energy distributions. Photoelectron images were processed by the pBASEX algorithm.<sup>4</sup>

A 20 Hz femtosecond Ti:Sa oscillator/amplifier chain was utilized for the experiments. In accordance with the absorption spectra of the carbenes, the third harmonic of the Ti:Sa laser (265 nm, 2  $\mu$ J) was used as the pump pulse. Following the initial excitation, the fundamental of the Ti:Sa (795 nm, 480  $\mu$ J) was used as the probe pulse in a multiphoton ionization process. Both laser beams were horizontally polarized. The pump-probe time delay was controlled by means of a delay line set on the pump beam and actuated by a computer-controlled stepper motor. The time intervals between two data points were not constant in a given time scan and adjusted to the slope of the decay signal. Around zero in time, data points were taken typically every 8 fs, whereas at early and late delay times, longer intervals were chosen. The beams were overlapped in a small angle and sent into the interaction region by a 700 mm lens for the 265 nm and a 500 mm lens for the 795 nm. The 795 nm were focused 5 cm away from the interaction region, the focus for the 265 nm was 14 cm away. For pump-probe contrast optimization the probe beam was attenuated by a polarizer until the one-color background signal was minimized. The laser cross correlation was typically around 100 fs. In the time-delay scans, 256 shots were averaged per data point. The time-resolved spectra reported here typically constitute an average of five such scans.

#### **b) Time of flight mass spectra/pyrolysis on**

In experiments on reactive intermediates it is important to ensure a clean generation of the species of interest. Therefore time-of-flight mass spectra were recorded in order to optimize carbene generation. Spectra of TFPC and CPC with the pyrolysis turned on are presented in figure S1. Only a very small

carbene signal is present without turning the pyrolysis on, originating from dissociative photoionization of the precursor. These carbene ions are distinguishable from the pyrolytically generated carbenes by velocity map imaging<sup>4</sup> due to a higher velocity spread. With pyrolysis off the ion signal intensities of CPC<sup>+</sup> and TFPC<sup>+</sup> are only 0.1 – 1 % of the intensity obtained with the pyrolysis turned on. In the CPC experiments a side product due to Cl loss in the pyrolysis is observed in small concentration.

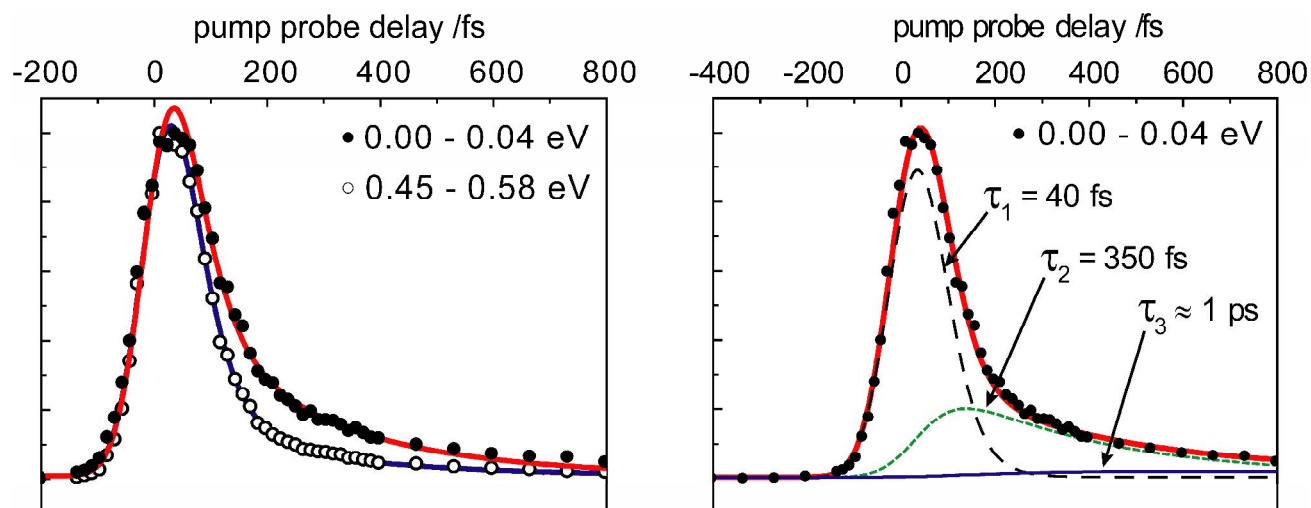


**Figure S1.** TOF-MS of chlorophenylcarbene (left) and trifluoromethylphenylcarbene (right) generated by jet flash pyrolysis of the corresponding diaziridine. Loss of chlorine is a side reaction in the pyrolytic generation of chlorophenylcarbene, while trifluoromethylphenylcarbene loses HF and CF<sub>3</sub> in a dissociative photoionisation.

Diazirines pyrolyse efficiently already at very low pyrolysis temperatures and are volatile enough to use high backing pressures, ensuring a cold molecular beam and fast expansion. When turning the pyrolysis on, the carbene signal strongly increases and the precursor is converted completely.

### c) Time-resolved photoelectron spectra

Time-resolved photoelectron spectra of CPC yield additional insight into the excited-state dynamics. On the left hand side of figure S2 the photoelectron signal at high kinetic energy (for example 0.45 eV-0.58 eV) is compared to the signal of near-threshold electrons (0.00-0.04 eV kinetic energy). Both time dependent signals are normalized to the same maximum intensity. Photoelectrons with a kinetic energy of around 0.5 eV (open circles) show the same time dependence as the CPC ion signal given in figure 1 of the paper. The time dependent signal can be perfectly described by two time constants (model: I→II→III) as indicated by a blue solid line ( $\tau_1=40$  fs,  $\tau_2=350$  fs). On the other hand the low kinetic energy electrons (0.00-0.04 eV) cannot be adequately described by the same two time constants (red line). The time dependent signal of the low kinetic energy electrons has to be described by a three-step decay process (I→II→III→IV) as depicted on the right hand side of figure S2. An additional time constant of  $\approx 1$  ps has to be included in the fit, although the amplitude is rather small. Note that several scans were recorded over a longer range of pump-probe delays, confirming the existence of this additional time constant. However, due to the larger step size, the fast time constant cannot be represented well in these measurements.



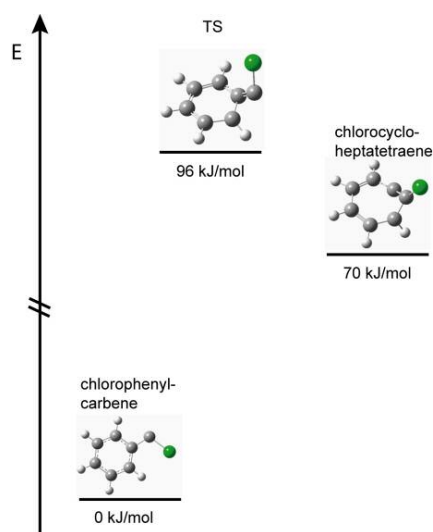
**Figure S2.** Time delay scans of chlorophenylcarbene recorded by TRPES. Electrons with very low kinetic energy show a different time dependence than electrons around 0.5 eV (left). For an adequate description of the time dependence of electrons with 0.00-0.04 eV three time constants are required. Their contributions to the total signal are given on the right hand side.

#### d) Possible Isomerization to chlorocycloheptatetraene in the pyrolysis

The mass spectra given in figure S1 show a complete conversion of the precursor. However, mass spectrometry cannot easily distinguish between isomers of the same mass. We therefore carried out *ab initio* calculations of the reaction between chlorophenylcarbene and chlorocycloheptatetraene. The BMK functional and a 6-311<sup>++G</sup> basis set were employed in the calculations.<sup>5</sup> They predict the chlorophenylcarbene to be 70 kJ/mol lower in energy than the corresponding chlorocycloheptatetraene. The barrier for the isomerization to chlorocycloheptatetraene was calculated by QST3/BMK/6-311<sup>++G</sup> to lie at 96 kJ/mol (compare figure 3). Thus the pyrolysis will produce CPC and isomerization to chlorocycloheptatetraene can be ruled out on thermochemical grounds.

## e) Supporting Calculations

- **Isomerization to cycloheptatetraene (BMK/6-311++G\*\* QST3):** The calculations depicted in figure S3 were performed using Gaussian 03.<sup>6</sup>



**Figure S3.** Isomerization of chlorophenylcarbene to chlorocycloheptatetraene as a possible side reaction in the pyrolysis. The BMK/6-311++G\*\* calculation shows that the carbene is thermodynamically favored.

-chlorophenylcarbene geometry (0 imaginary frequencies)

(Sum of electronic and zero-point energies = -729.505469 ha, E(RBMK+HF-BMK) = -729.600772678 ha):

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.404516	-0.992205	0.000000
2	6	0	-0.084563	-0.370632	0.000000
3	6	0	0.247327	1.007917	0.000000
4	6	0	0.962138	-1.322371	0.000001
5	6	0	1.575063	1.406104	0.000000
6	1	0	-0.546506	1.747072	-0.000001
7	6	0	2.295590	-0.919220	0.000002
8	1	0	0.689998	-2.373307	0.000001
9	6	0	2.598203	0.443684	0.000001
10	1	0	1.828126	2.461575	0.000000
11	1	0	3.092695	-1.655500	0.000003
12	1	0	3.635498	0.766287	0.000002
13	17	0	-2.696192	0.207895	-0.000002

-TS geometry (1 imaginary frequency)

(Sum of electronic and zero-point energies = -729.469084 ha, E(RBMK+HF-BMK) = -729.562845316 ha):

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.198674	-0.527427	0.663181
2	6	0	-0.051752	0.117972	0.949928
3	6	0	0.665862	1.314884	0.660023
4	6	0	0.432013	-1.226395	0.619063
5	6	0	1.739646	1.191617	-0.175677
6	1	0	0.317834	2.276787	1.020386
7	6	0	1.494554	-1.248746	-0.364111
8	1	0	0.280909	-2.092064	1.247603
9	6	0	2.104266	-0.083332	-0.740037
10	1	0	2.298612	2.073304	-0.473349
11	1	0	1.871594	-2.203502	-0.718761
12	1	0	2.932054	-0.114935	-1.442317
13	17	0	-2.283323	0.166410	-0.547517

-chlorocycloheptatetraene geometry (0 imaginary frequencies):  
 (Sum of electronic and zero-point energies= -729.478941ha, E(RBMK+HF-BMK) = -729.572858980)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.943721	-0.091506	0.441886
2	6	0	-0.094470	-0.812987	0.675040
3	6	0	-1.280019	-1.477496	0.268065
4	6	0	-0.046261	0.878130	0.955062
5	6	0	-2.110743	-0.695202	-0.483576
6	1	0	-1.513401	-2.498570	0.547905
7	6	0	-1.020621	1.480326	0.050364
8	1	0	0.075102	1.291520	1.956484
9	6	0	-1.902498	0.724629	-0.675821
10	1	0	-3.013633	-1.131661	-0.901675
11	1	0	-1.141217	2.562564	0.050245
12	1	0	-2.610882	1.240234	-1.317799
13	17	0	2.427610	-0.088203	-0.454193

-Frequencies:

Chlorophenylcarbene /cm <sup>-1</sup>	TS /cm <sup>-1</sup>	Chlorocycloheptatetraene /cm <sup>-1</sup>
3226.4074	3243.4171	3204.5982
3212.2277	3206.4929	3192.4558
3196.6141	3198.0930	3175.7357
3191.8318	3182.8376	3154.3745
3177.4613	3173.8902	3115.9624
1632.3916	1666.2013	1904.6359
1608.8926	1606.8142	1618.2017
1517.8512	1511.0969	1512.8292
1475.3693	1460.4194	1458.8125
1361.5434	1393.5736	1402.9794
1318.5636	1326.3234	1342.9985
1245.9320	1204.0342	1236.1164
1212.9796	1194.3534	1205.7272
1187.2687	1161.2866	1170.6591
1117.3313	1097.1483	1054.2456
1049.5643	1019.0415	1018.6357
1046.5098	1004.2947	1001.9691
1028.6125	985.5583	968.3020
1013.1943	960.8760	957.2299
998.3992	932.6661	930.4177
880.2685	855.2237	894.6083
864.0732	811.8191	821.0715
801.0322	785.1409	736.8720
768.7281	741.0920	664.2535
700.2308	679.0151	634.5080
622.3488	601.6772	619.6414
578.3365	573.3659	518.9159
474.7507	526.7536	454.7251
418.3432	410.0179	432.1202
366.7660	333.6351	372.7983
231.3948	214.6778	190.6958
227.2076	95.5648	165.1988
80.8381	i253.0524	93.0772

- **Time-dependent DFT calculations:**

Calculations of the excited state characteristics and the vertical excitation energies were performed by time-dependent density functional theory (TD-DFT) as implemented in Gaussian 03. A full optimization for the ground state equilibrium geometry was carried out at the B3LYP/6-311<sup>++</sup>G<sup>\*\*</sup> level of theory in C<sub>s</sub> symmetry:

-chlorophenylcarbene geometry (0 imaginary frequencies)  
 (Sum of electronic and zero-point Energies= -729.846555 ha, E(RB+HF-LYP) = -729.941030184 ha):

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.40312	-0.98179	0.000000
2	6	0	0.08606	-0.37027	0.000000
3	6	0	-0.24979	1.00512	0.000000
4	6	0	-0.9609	-1.31998	0.000000
5	6	0	-1.57533	1.40226	0.000000
6	1	0	0.54136	1.74435	0.000000
7	6	0	-2.29127	-0.91814	0.000000
8	1	0	-0.689	-2.36883	0.000000
9	6	0	-2.59589	0.44195	0.000000
10	1	0	-1.82804	2.45646	0.000000
11	1	0	-3.08576	-1.655	0.000000
12	1	0	-3.63217	0.76239	0.000000
13	17	0	2.69398	0.20622	0.000000

This geometry was used in the TD-B3P86/6-311++g\*\* calculations for the excited states:

Excited State 1: Singlet-A"	1.5359 eV	807.25 nm	f=0.0014
32 -> 33	0.61531		
Excited State 2: Singlet-A'	3.9357 eV	315.03 nm	f=0.0227
30 -> 34	0.15912		
31 -> 33	0.65496		
Excited State 3: Singlet-A"	4.0877 eV	303.31 nm	f=0.0002
32 -> 34	0.70553		
Excited State 4: Singlet-A'	4.4595 eV	278.03 nm	f=0.3322
30 -> 33	0.61414		
31 -> 34	-0.11818		
Excited State 5: Singlet-A"	4.7556 eV	260.71 nm	f=0.0000
29 -> 33	0.68376		
32 -> 35	0.13853		
Excited State 6: Singlet-A"	5.0268 eV	246.65 nm	f=0.0065
29 -> 33	-0.12405		
32 -> 35	0.66969		

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