

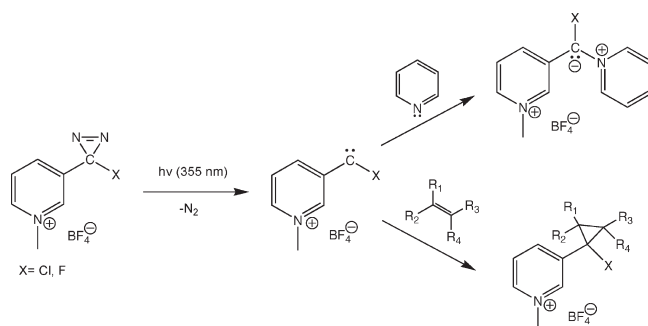
## Reactivity of Halo(pyridinium)carbenes

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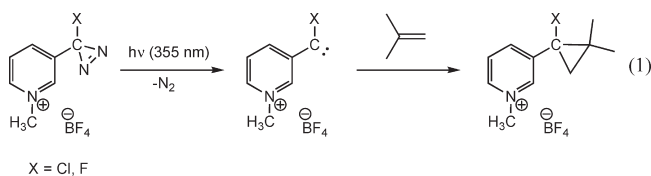
The reactivity of chloro- and fluoro(*N*-methyl-3-pyridinium)carbenes was examined by laser flash photolysis, where the halo(pyridinium)carbenes formed ylides with pyridine, acetonitrile, and acetone. Although the halo(pyridinium)carbenes reacted within the time of the laser pulse, their relative reactivities with a series of alkenes could be obtained from quenching experiments by using carbene–pyridine ylides. Their relative order of reactivity with the alkenes and their poor overall selectivity showed that the halo(pyridinium)carbenes are strongly reactive electrophilic species. Computational studies demonstrated that the alkene (HOMO)–carbene (LUMO) interaction is predominant in halo(pyridinium)carbene–alkene reactions, supporting the electrophilic nature of these species.

### Introduction

Heteroarylcabenenes have received attention due to their potential use in the synthesis of indolizines and heteroaryl-cyclopropanes that can be precursors in the synthesis of novel heterocyclic compounds.<sup>1</sup> Among these, halo(pyridyl)carbenes are ambiphilic species known for their increased reactivity compared to the well-known halo(phenyl)carbenes.<sup>2,3</sup> The high reactivity of the halo(pyridyl)carbenes is largely dictated by the presence of the electron-withdrawing pyridine ring.

Moss and co-workers have provided evidence that halo-(pyridinium)carbenes, which are expected to be even more electron-deficient than the pyridine analogues, are generated upon irradiation of 3-halo-3-(*N*-methyl-3-pyridinium)diazirines.<sup>2</sup> In their work, it was shown that steady-state photolysis of 3-chloro-3-(*N*-methyl-3-pyridinium)diazirine tetrafluoroborate or

3-fluoro-3-(*N*-methyl-3-pyridinium)diazirine tetrafluoroborate in isobutene/acetone solution produced the corresponding halocyclopropanes, presumably by addition of the chloro(*N*-methyl-3-pyridinium)carbene or fluoro(*N*-methyl-3-pyridinium)carbene to the alkene, eq 1.

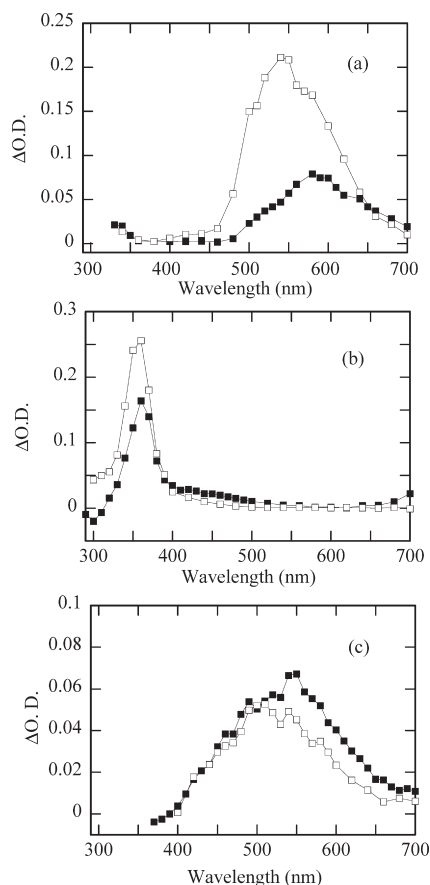


In the present work, we study the reactivity of halo(*N*-methyl-3-pyridinium)carbenes in solution by laser flash photolysis (LFP) of the corresponding diazirines in order to investigate the effect of the strongly electron-withdrawing pyridinium group on carbene reactivity. Spectral features of the carbene ylides formed with different Lewis bases as well as carbene reactivity toward a series of alkenes were examined. The discussion is based on the experimental

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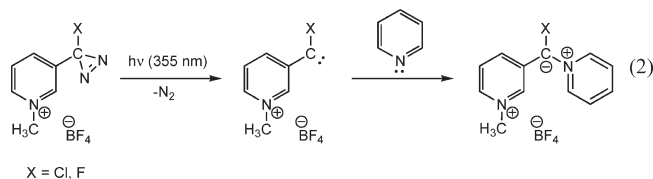
**FIGURE 1.** Transient spectra obtained upon 355 nm laser irradiation of (■) 3-chloro-3-(*N*-methyl-3-pyridinium)diazirine tetrafluoroborate (0.0011 M), and (□) 3-fluoro-3-(*N*-methyl-3-pyridinium)diazirine tetrafluoroborate (0.0010 M) at 22 °C in (a) 1:1 dichloromethane–pyridine (1.60  $\mu$ s after the excitation pulse), (b) acetonitrile (2.30  $\mu$ s after the excitation pulse), and (c) acetone (28 ns after the excitation pulse).

results as well as on theoretical calculations on halo(*N*-methyl-3-pyridinium)carbenes.

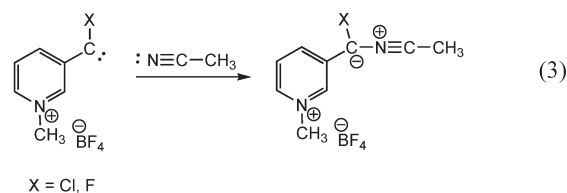
### Generation of Halo(pyridinium)carbenes

Nanosecond laser flash photolysis of 3-chloro-3-(*N*-methyl-3-pyridinium)diazirine (3-CH<sub>3</sub>Py<sup>+</sup>ClCN<sub>2</sub>) as the tetrafluoroborate salt in dichloromethane produced no visible transient absorption signal above 300 nm. However, laser irradiation of the diazirine in a 1:1 dichloromethane–pyridine mixture produced a spectrum dominated by an intense absorption band centered at 600 nm that decayed with a first-order rate constant of  $1.3 \times 10^3 \text{ s}^{-1}$  ( $\tau = 700 \mu\text{s}$ ), Figure 1a. The broad shape and position of this band along with its long lifetime is typical of carbene–pyridine ylides.<sup>4–6</sup> For example, the ylide of the very electron-deficient chloro(4-nitrophenyl)carbene with pyridine absorbs similarly at 605 nm.<sup>7</sup> Laser photolysis of 3-CH<sub>3</sub>Py<sup>+</sup>ClCN<sub>2</sub>

in dichloromethane containing variable amounts of pyridine produced a gradual increase of the intensity of the transient at 600 nm, Figure 2. This result indicates that the absorption at 600 nm depends strongly on the concentration of pyridine. From these results, the absorption band at 600 nm can be confidently identified as the carbene–pyridine ylide formed upon reaction of the photogenerated chloro(*N*-methyl-3-pyridinium)carbene (3-CH<sub>3</sub>Py<sup>+</sup>ClC:) with pyridine, eq 2 (X = Cl). Under all concentrations of pyridine the absorption band at 600 nm due to formation of the ylide formed promptly within the nanosecond laser pulse.



In acetonitrile, 355 nm laser irradiation of 3-CH<sub>3</sub>Py<sup>+</sup>ClCN<sub>2</sub> produced the “prompt” formation of a long-lived transient with an absorption maximum at 360 nm that decayed with a rate constant of  $4.0 \times 10^4 \text{ s}^{-1}$  ( $\tau = 25 \mu\text{s}$ ), Figure 1b. The narrow shape and position of the absorption band in the 320–400 nm region of the spectrum is typical of other carbene–acetonitrile ylides, such as those formed by 1-naphthyl<sup>8,9</sup> and 2-naphthylcarbenes,<sup>10</sup> fluoren-9-ylidene,<sup>11</sup> and cyclopentadienylidene.<sup>12</sup> On the basis of these similarities, it is reasonable to conclude that the absorption band at 360 nm corresponds to the carbene–acetonitrile ylide formed upon the reaction of 3-CH<sub>3</sub>Py<sup>+</sup>ClC:<sup>+</sup> with the acetonitrile solvent, eq 3 (X = Cl).



Laser irradiation of 3-CH<sub>3</sub>Py<sup>+</sup>ClCN<sub>2</sub> in neat acetone produced a broad and intense absorption band centered at 550 nm, Figure 1c. The transient absorption was assigned to the ylide of 3-CH<sub>3</sub>Py<sup>+</sup>ClC: with acetone, eq 4 (X = Cl). This assignment was based on several observations. The broad shape of the transient absorption band at 550 nm closely resembles that of other carbene–acetone ylides, and its absorption maximum was intermediate between the acetone ylides of similarly electron-deficient chloro(4-trifluoromethylphenyl)carbene ( $\lambda_{\text{max}} = 480 \text{ nm}$ ) and chloro(4-nitrophenyl)carbene ( $\lambda_{\text{max}} = 590 \text{ nm}$ ).<sup>13,14</sup> Moreover, the transient at 550 nm decayed quickly with a first-order rate constant of  $1.3 \times 10^6 \text{ s}^{-1}$  ( $\tau = 770 \text{ ns}$ ), consistent with the previously reported

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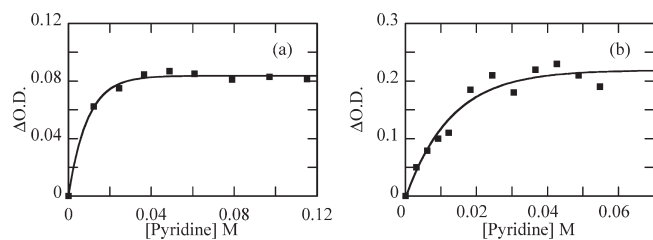
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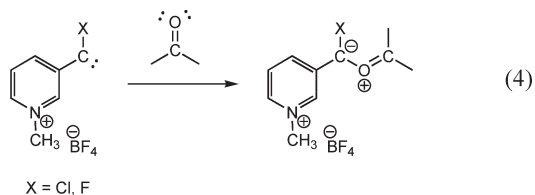
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**FIGURE 2.** Variation in  $\Delta O.D.$  as a function of the concentration of pyridine upon 355 nm laser irradiation of (a) 3-chloro-3-(*N*-methyl-3-pyridinium)diazirine tetrafluoroborate (0.0011 M) at 600 nm and (b) 3-fluoro-3-(*N*-methyl-3-pyridinium)diazirine tetrafluoroborate (0.0010 M) at 540 nm, in air-saturated dichloromethane.

reactivity of other carbene–acetone ylides.<sup>9,12,15</sup> In particular, the closely related chloro(aryl)carbenes produced carbene–acetone ylides with lifetimes shorter than 1.5  $\mu$ s.<sup>13,14</sup>



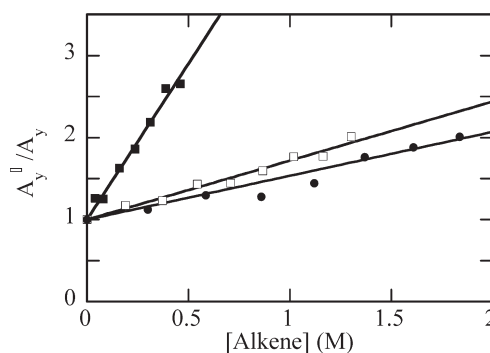
Results from laser experiments with 3-fluoro-3-(*N*-methyl-3-pyridinium)diazirine (3-CH<sub>3</sub>Py<sup>+</sup>FCN<sub>2</sub>) as the tetrafluoroborate salt closely resemble those obtained for the chloro derivative. Laser irradiation of 3-CH<sub>3</sub>Py<sup>+</sup>FCN<sub>2</sub> in dichloromethane showed no absorption in the 300–700 nm region in the UV–vis spectrum, but laser irradiation in a 1:1 pyridine–dichloromethane solution yielded a transient with strong and broad absorption centered at 540 nm, Figure 1a. This transient formed within the time of the laser pulse and decayed with a rate constant of  $1.6 \times 10^4 \text{ s}^{-1}$  ( $\tau = 63 \mu\text{s}$ ). The yield of this species at 540 nm was dependent on the concentration of pyridine, Figure 2b, and was accordingly attributed to the carbene–pyridine ylide obtained by trapping of the fluoro(*N*-methyl-3-pyridinium)carbene (3-CH<sub>3</sub>-Py<sup>+</sup>FC:) with pyridine, eq 2 (X = F).

Laser irradiation of 3-CH<sub>3</sub>Py<sup>+</sup>FCN<sub>2</sub> in acetonitrile led to the formation of a narrow and intense absorption band centered at 360 nm, Figure 1b, that decayed with a first-order rate constant of  $6.6 \times 10^3 \text{ s}^{-1}$  ( $\tau = 150 \mu\text{s}$ ) and was assigned to the 3-CH<sub>3</sub>Py<sup>+</sup>FC:–acetonitrile ylide, eq 3 (X = F). Furthermore, in neat acetone, laser flash photolysis of 3-CH<sub>3</sub>-Py<sup>+</sup>FCN<sub>2</sub> produced an absorption spectrum containing one broad absorption band at 510 nm that decayed in a simple first-order manner with a rate constant of  $1.0 \times 10^7 \text{ s}^{-1}$  ( $\tau = 100 \text{ ns}$ ), Figure 1c. The short lifetime and the position and shape of the absorption band permitted identification of this transient as the carbene–acetone ylide formed by the addition of 3-CH<sub>3</sub>Py<sup>+</sup>FC: to acetone, eq 4 (X = F).

### Reactivity of Halo(pyridinium)carbenes with Alkenes

The spectral evidence with pyridine indicates that the halo(pyridinium)carbenes 3-CH<sub>3</sub>Py<sup>+</sup>ClC: and 3-CH<sub>3</sub>Py<sup>+</sup>FC: are highly reactive and in dichloromethane decay faster than the time resolution of our laser system,  $k_{\text{decay}} \geq 5 \times 10^7 \text{ s}^{-1}$ . As such,

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**FIGURE 3.** Stern–Volmer plot for the quenching of chloro(*N*-methyl-3-pyridinium)carbene–pyridine ylide as a function of the concentration of (■) 2,3-dimethyl-2-butene, (□) 1-hexene, and (●) 2-chloroacrylonitrile, in the presence of 0.047 M of pyridine in air-saturated dichloromethane.

neither the absolute rate constant for the decay of the carbene nor the bimolecular rate constant for the reaction with quenchers can be directly determined. However, the relative reactivity of the halo(*N*-methyl-3-pyridinium)carbenes toward a series of alkenes can be estimated by the competition method developed by Platz and co-workers.<sup>16</sup> Stern–Volmer plots of each alkene are constructed at concentrations of pyridine sufficiently large such that, in the absence of the alkene quencher, the optical density of the carbene–pyridine ylide ( $A_y$ ) equals the maximum (or saturation) optical yield of ylide ( $A_y^\infty$ ), eq 5. The approximate saturation concentration of pyridine was obtained from a graph of the variation of  $A_y$  at 600 nm as a function of pyridine concentration, Figure 2. For both 3-CH<sub>3</sub>Py<sup>+</sup>ClC: and 3-CH<sub>3</sub>Py<sup>+</sup>FC:, the pyridine saturation concentration exceeds 0.04 M.

$$\frac{A_y^\infty}{A_y} = 1 + \frac{k_Q[\text{alkene}]}{k_{\text{pyr}}[\text{pyridine}]} \quad (5)$$

According to eq 5, a plot of  $A_y^\infty/A_y$  as a function of [alkene] at [pyridine] higher than the saturation concentration should be linear, and from the slope it is possible to obtain the ratio  $k_Q/k_{\text{pyr}}$ , Figure 3. The relative rates of addition of the halo(pyridinium)carbenes to the alkenes with respect to 1-hexene ( $k_Q/k_Q(1\text{-hexene})$ ) were determined by dividing the slopes from the Stern–Volmer plots for each alkene by that of 1-hexene. These values along with the  $k_Q/k_Q(1\text{-hexene})$  values reported in the literature for the chloro-(3-pyridyl)carbene (3-PyClC:) and fluoro(3-pyridyl)carbene (3-PyFC:) in isooctane are shown in Table 1.<sup>2,3,17,18</sup>

The ylides formed from the highly electron deficient halo(pyridinium)carbenes with pyridine are significantly red-shifted compared to those ylides composed of halo(pyridyl)carbenes with pyridine, and have absorption maxima that are similar to that of the highly reactive chloro(4-nitrophenyl)carbene.<sup>7</sup>

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(17) Relative values for chloro(3-pyridyl)- and fluoro(3-pyridyl)carbenes with *trans*-2-hexene in isooctane were calculated by using the experimentally obtained bimolecular rate constants of  $4.2 \times 10^7$  and  $2.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , respectively.

(18) Relative values for chloro(3-pyridyl)- and fluoro(3-pyridyl)carbenes with acrylonitrile in isooctane were calculated by using the experimentally obtained bimolecular rate constants of  $2.2 \times 10^7$  and  $1.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , respectively.

**TABLE 1.** Relative Rate Constants with Respect to Pyridine ( $k_Q/k_{\text{pyr}}$ ) and 1-Hexene ( $k_Q/k_Q(1\text{-hexene})$ ) for the Addition of Halo(*N*-methyl-3-pyridinium)carbenes to Alkenes in Dichloromethane along with Relative Reactivities of Halo(3-pyridyl)carbenes with Alkenes (in isooctane) for Comparison

alkene	$k_Q/k_{\text{pyr}}$		$k_Q/k_Q(1\text{-hexene})$			
	3-CH <sub>3</sub> Py <sup>+</sup> CIC:	3-CH <sub>3</sub> Py <sup>+</sup> FC:	3-CH <sub>3</sub> Py <sup>+</sup> CIC:	3-CH <sub>3</sub> Py <sup>+</sup> FC:	3-PyCIC:	3-PyFC:
Me <sub>2</sub> C=CMe <sub>2</sub>	0.27	0.50	3.9	4.7	76 <sup>a</sup> (67) <sup>b</sup>	179 <sup>a</sup>
Me <sub>2</sub> C=CHMe	0.24	0.40	3.6	3.7	45 <sup>a</sup> (29) <sup>b</sup>	72 <sup>a</sup>
<i>trans</i> - <i>n</i> -PrC=CHMe	0.11	0.20	1.6	2.0	4.6 <sup>c</sup>	7.2 <sup>c</sup>
<i>n</i> -BuCH=CH <sub>2</sub>	0.068	0.11	1	1	1	1
CH <sub>2</sub> =CHCO <sub>2</sub> Me	0.045	0.075	0.66	0.70	1.6 <sup>a</sup>	9.3 <sup>a</sup>
CH <sub>2</sub> =CHCN	0.026	0.064	0.38	0.60	2.4 <sup>d</sup> (3.1) <sup>b</sup>	5.8 <sup>d</sup>
CH <sub>2</sub> =CClCN	0.030	0.060	0.44	0.56	32 <sup>a</sup> (31) <sup>b</sup>	52 <sup>a</sup>

<sup>a</sup>Data from ref 3. <sup>b</sup>Data from ref 2. <sup>c</sup>Data from ref 17. <sup>d</sup>Data from ref 18.

**TABLE 2.** Estimated Bimolecular Rate Constants ( $k_Q^*$ ) for the Addition of Chloro(*N*-methyl-3-pyridinium)carbene to a Series of Alkenes in dichloromethane<sup>a</sup>

alkene	$k_Q^*/10^8 \text{ M}^{-1} \text{ s}^{-1}$
Me <sub>2</sub> C=CMe <sub>2</sub>	20
Me <sub>2</sub> C=CHMe	18
<i>trans</i> - <i>n</i> -PrC=CHMe	8.3
<i>n</i> -BuCH=CH <sub>2</sub>	5.1
CH <sub>2</sub> =CHCO <sub>2</sub> Me	3.3
CH <sub>2</sub> =CHCN	2.0
CH <sub>2</sub> =CClCN	2.2

<sup>a</sup>Estimated rate constants were calculated assuming  $k_{\text{pyr}} = 7.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

Furthermore, halo(pyridinium)carbenes readily form ylides with acetonitrile and acetone, which is only typical of highly reactive carbenes.<sup>13,14,19</sup> This pattern of reactivity resembles closely that of the very electron-deficient chloro(4-nitrophenyl)carbene. Therefore, it seems reasonable to estimate that the bimolecular rate constant for the reaction of the 3-CH<sub>3</sub>Py<sup>+</sup>CIC: with pyridine  $k_Q$  is closely similar to the bimolecular rate constant for the reaction of the chloro(4-nitrophenyl)carbene with pyridine ( $7.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>7</sup> For each reaction with pyridine the carbenes contain a highly electron deficient ring and also a chlorine substituent attached to the carbene center. On the basis of this assumption for  $k_{\text{pyr}}$ , and using the ratios  $k_Q/k_{\text{pyr}}$  obtained from the Stern–Volmer plots (Table 1), the bimolecular quenching rate constants  $k_Q^*$  for the chloro(*N*-methyl-3-pyridinium)carbene–alkene addition reactions can be estimated, Table 2. A similar estimation for the 3-CH<sub>3</sub>Py<sup>+</sup>FC: is not made as the reactivity of the fluoro(4-nitrophenyl)carbene with pyridine has not been reported.

However, the higher selectivity observed for the reactions of 3-CH<sub>3</sub>Py<sup>+</sup>FC: with the series of alkenes studied suggests that the bimolecular rate constants will have somewhat lower values than those reported in Table 2 for the 3-CH<sub>3</sub>Py<sup>+</sup>CIC:.

### Theoretical Calculations on Halo(pyridinium)carbenes

Geometry optimization at the B3LYP/6-31G\* level of theory of halo(pyridinium)carbenes predicts the structural parameters shown in Table 3. The computed carbenic angles (X–C–C) of 3-CH<sub>3</sub>Py<sup>+</sup>CIC: and 3-CH<sub>3</sub>Py<sup>+</sup>FC: closely resemble those of the halo(pyridyl)carbenes, and are consistent with the reported angles for singlet ground state carbenes.<sup>20</sup> More importantly, the  $d(\text{C}(\text{carbenic})\text{--C})$  bond lengths for

**TABLE 3.** Theoretical Calculations at the B3LYP/6-31G\* Level of Theory X–C–C Angles, Carbenic Carbon–Carbon, and Halogen–Carbon Bond Distances in Halo(*N*-methyl-3-pyridinium)carbenes and Halo(3-pyridyl)carbenes in the Gas Phase

carbene	$\angle \text{X–C–C}$ (deg)	$d(\text{C}(\text{carbenic})\text{--C})$ (Å)	$d(\text{X–C})$ (Å)
3-CH <sub>3</sub> Py <sup>+</sup> CIC:	111.7	1.485	1.706
3-PyCIC:	111.6	1.455	1.763
3-CH <sub>3</sub> Py <sup>+</sup> FC:	106.2	1.511	1.314
3-PyFC:	107.0	1.470	1.344

halo(pyridinium)carbenes are significantly longer, while the halogen–carbon bonds are considerably shorter, than those of the halo(pyridyl)carbenes.

Time-dependent density functional (TD-DFT) calculations were also carried out with the optimized structures of 3-CH<sub>3</sub>Py<sup>+</sup>CIC: and 3-CH<sub>3</sub>Py<sup>+</sup>FC:. In dichloromethane, 3-CH<sub>3</sub>Py<sup>+</sup>CIC: is predicted to have an absorption maximum ( $\pi \rightarrow \pi^*$ ) at 278 nm with an oscillator strength ( $f$ ) of 0.1902. On the other hand, the fluoro derivative, 3-CH<sub>3</sub>Py<sup>+</sup>FC:, is predicted to absorb at 257 nm ( $\pi \rightarrow \pi^*$ ,  $f = 0.1158$ ) in dichloromethane. In both cases, the calculated absorption bands for the halo(pyridinium)carbenes are outside the experimental detection region ( $> 300 \text{ nm}$ ).

The HOMO and LUMO energies for the halo(pyridinium)carbenes were also computed. For 3-CH<sub>3</sub>Py<sup>+</sup>CIC:, the energy of the HOMO is  $-10.099 \text{ eV}$  and the energy of the LUMO is  $-7.732 \text{ eV}$ . Similar values were obtained for 3-CH<sub>3</sub>Py<sup>+</sup>FC:, with HOMO and LUMO energies of  $-10.457$  and  $-7.619 \text{ eV}$ , respectively. These values were used to calculate the LUMO–HOMO differential energies for the addition of the halo(*N*-methyl-3-pyridinium)carbenes to the alkenes shown in Table 4.<sup>21</sup>

### Discussion

The spectral evidence presented indicates that halo(pyridinium)carbenes are photogenerated upon laser flash photolysis of their diazirine precursors. Although the halo(pyridinium)carbenes were not directly detected in dichloromethane, acetonitrile, or acetone, evidence of carbene formation was indirectly obtained from the formation of ylides with pyridine, acetonitrile, and acetone. In each case, ylide formation took place very quickly within the time frame of the laser pulse, which indicates that the halo(pyridinium)carbenes are very reactive species with decay rate constants in dichloromethane greater than the time

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**TABLE 4.** LUMO Carbene/HOMO Alkene ( $p-\pi$ ) and LUMO Alkene/HOMO Carbene ( $\pi^*-\sigma$ ) Differential Energies (in eV)<sup>21</sup> for the Addition of Halo(*N*-methyl-3-pyridinium)carbenes and Halo(3-pyridyl)carbenes to Alkenes in the Gas Phase Calculated at the B3LYP/6-31G\* Level of Theory<sup>a</sup>

alkenes	carbenes							
	3-CH <sub>3</sub> Py <sup>+</sup> CIC:		3-CH <sub>3</sub> Py <sup>+</sup> FC:		3-PyCIC:		3-PyFC:	
	$p-\pi$	$\pi^*-\sigma$	$p-\pi$	$\pi^*-\sigma$	$p-\pi$	$\pi^*-\sigma$	$p-\pi$	$\pi^*-\sigma$
Me <sub>2</sub> C=CMe <sub>2</sub>	<b>-1.80</b>	11.1	<b>-1.69</b>	11.5	<b>2.66</b>	7.06	<b>3.10</b>	7.11
Me <sub>2</sub> C=CHMe	<b>-1.59</b>	11.1	<b>-1.48</b>	11.5	<b>2.87</b>	7.08	<b>3.31</b>	7.13
<i>trans</i> - <i>n</i> -PrC=CHMe	<b>-1.34</b>	11.0	<b>-1.23</b>	11.3	<b>3.12</b>	6.90	<b>3.56</b>	6.95
<i>n</i> -BuCH=CH <sub>2</sub>	<b>-0.971</b>	10.8	<b>-0.857</b>	11.2	<b>3.49</b>	6.77	<b>3.94</b>	6.82
CH <sub>2</sub> =CHCO <sub>2</sub> Me	<b>-0.309</b>	11.3	<b>-0.196</b>	11.7	<b>4.15</b>	4.84	<b>4.60</b>	4.89
CH <sub>2</sub> =CHCN	<b>0.157</b>	8.57	<b>0.271</b>	8.92	4.62	<b>4.51</b>	5.06	<b>4.56</b>
CH <sub>2</sub> =CClCN	<b>0.131</b>	8.18	<b>0.244</b>	8.54	4.59	<b>4.13</b>	5.04	<b>4.18</b>

<sup>a</sup>The bold numbers represent the predominant carbene–alkene interaction.

resolution of our laser system,  $k_{\text{decay}} \geq 5 \times 10^7 \text{ s}^{-1}$ . Since intramolecular rearrangements are unlikely for these carbenes the halo(pyridinium)carbenes presumably decay in the absence of quencher by intermolecular processes, such as insertion reactions with the solvent and reaction with their diazine precursors.

The ability of halo(pyridinium)carbenes to produce ylides with acetonitrile, as well as the position of the absorption maxima of their pyridine and acetone ylides, not only demonstrates carbene formation but also strongly suggests that the reactivity of the halo(pyridinium)carbenes resembles that of other very electron-deficient carbenes such as chloro-(4-nitrophenyl)carbene. Among chloro(phenyl)carbenes, only the very electron-deficient chloro(4-nitrophenyl)carbene<sup>19</sup> is known to form ylides with acetonitrile. Moreover, the absorption maxima of the 3-CH<sub>3</sub>Py<sup>+</sup>CIC: pyridine and acetone ylides are very similar to those ylides of the chloro(4-nitrophenyl)carbene.<sup>7,14</sup>

The absorption maximum of 600 nm the 3-CH<sub>3</sub>Py<sup>+</sup>CIC: pyridine ylide is red-shifted more than 100 nm compared to that of the closely related 3-PyCIC: ylide formed with its pyridine-like precursor ( $\lambda_{\text{max}} = 480 \text{ nm}$ ).<sup>2</sup> This result is consistent with the greater electron-withdrawing power of the pyridinium group compared to the pyridyl group. The introduction of an electron-withdrawing substituent is well-known to shift the absorption maximum of the carbene ylides to longer wavelengths. For example, the absorption maximum of the chloro(phenyl)carbene–pyridine ylide is centered a 475 nm while that of chloro(4-nitrophenyl)carbene is centered at 605 nm.<sup>4,7</sup>

The data in Table 1 show that halo(pyridinium)carbenes exhibit a narrow range of relative rate constants with a series of alkenes. The reactivities of 3-CH<sub>3</sub>Py<sup>+</sup>CIC: and 3-CH<sub>3</sub>Py<sup>+</sup>FC: with 2,3-dimethyl-2-butene, the most electron-rich alkene in the series, are only 3.9 and 4.7 times faster, respectively, than their reaction with 1-hexene. In contrast, 3-PyCIC: and 3-PyFC: react 76 and 179 times faster, respectively, with 2,3-dimethyl-2-butene than with 1-hexene. Assuming a “classical” reactivity–selectivity pattern, these results clearly indicate that halo(*N*-methyl-3-pyridinium)carbenes are much more reactive than the corresponding halo(3-pyridyl)carbenes.

More importantly, the data in Table 1 show that the relative rate constants for the reactions of the halo(pyridinium)carbenes with electron-rich alkenes are faster than the relative rate constants for reaction with electron-deficient alkenes. As such, the reactivity of these carbenes follows a typical electrophilic pattern where the relative rate

constant decreases as the alkenes become more electron-deficient in nature. This contrasts with the previously reported ambiphilic behavior of halo(pyridyl)carbenes where the rate constants are faster for both electron-rich and electron-deficient alkenes.<sup>2,3</sup>

From this work the estimated rate constants for the reaction of the chloro(*N*-methyl-3-pyridinium)carbene with electron-rich alkenes are faster than those for the chloro(3-pyridyl)carbene, Table 2.<sup>2</sup> For example, the reaction of 3-CH<sub>3</sub>Py<sup>+</sup>CIC: with 1-hexene is estimated to be almost 60 times faster than that of 3-PyCIC:.

The heightened reactivity of halo(pyridinium)carbenes can be explained by the strong electron-withdrawing inductive effect of the positively charged pyridinium ring. The pyridinium ring makes these carbenes even more electron deficient and thus increases their reactivity. This is consistent with the well-known strategy for making a pyridine ring much more electron deficient through methylation of the pyridine nitrogen. The electron-deficient nature of the pyridinium ring increases its susceptibility toward nucleophilic attack.<sup>22</sup> For example, 3-chloro-*N*-methylpyridinium iodide reacts  $\sim 2.9 \times 10^8$  faster than 3-chloropyridine with sodium methoxide.<sup>23</sup>

The computational results show that the bond between the carbenic carbon and the aromatic carbon is substantially elongated in halo(*N*-methyl-3-pyridinium)carbenes relative to halo(3-pyridyl)carbenes, consistent with the reduced resonance electron-donating ability expected from the pyridinium ring. This is accompanied by a dramatic decrease in the C–X bond length that suggests a higher electronic demand of the very electron-deficient carbenic center, a result of the combination of strong electron-withdrawing inductive and poor electron-donating mesomeric effects of the pyridinium ring. Overall, the results indicate a lower stabilization of the carbene center of halo(*N*-methyl-3-pyridyl)carbenes as a consequence of the pyridinium substituent.

The low LUMO energies calculated for the halo(*N*-methyl-3-pyridyl)carbenes are consistent with the high reactivity and electrophilic behavior observed in these species. In addition, the HOMO energies of halo(pyridinium)carbenes are also significantly lower than those reported for halo(pyridyl)carbenes,<sup>3</sup> rendering the HOMO inaccessible, and consequently precluding the electron donation.

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The electrophilicity of halo(pyridinium)carbenes is also evident from the calculated differential frontier molecular orbital energies in Table 4, which correlate neatly with the experimental order of reactivity observed for these species. Regardless of the electron-rich or electron-deficient nature of the alkene, the LUMO carbene/HOMO alkene interaction is clearly predominant. Even in the case of the most electron-deficient alkene studied, 2-chloroacrylonitrile, the magnitude of LUMO alkene/HOMO carbene energy gap prevents nucleophilic behavior on the carbene's part allowing the carbene to act only as an electrophile even with an electron-deficient alkene. This contrasts markedly with the reported ambiphilicity of halo(pyridyl)carbenes, which react as electrophiles with electron-rich alkenes but as nucleophiles with electron-deficient alkenes.<sup>2,3</sup>

## Conclusions

The results described demonstrate that halo(*N*-methyl-3-pyridinium)carbenes are formed upon laser irradiation of their corresponding diazirines precursors. Carbene identification was possible based on the observed reactivity of these species that readily formed ylides with pyridine, acetonitrile, and acetone. In contrast with the well-established ambiphilicity of halo(pyridyl)carbenes, halo(*N*-methyl-3-pyridinium)carbenes followed a typical electrophilic reactivity pattern in their reaction with alkenes. The scant selectivity observed in their reactions with alkenes indicates that halo(*N*-methyl-3-pyridinium)carbenes are very reactive species. Computational studies corroborate that the higher reactivity of these carbenes

can be attributed to the presence of the strongly electron-withdrawing pyridinium ring.

## Experimental Section

**Materials.** The synthesis of 3-chloro-3-(*N*-methyl-3-pyridinium)diazirine tetrafluoroborate and 3-fluoro-3-(*N*-methyl-3-pyridinium)diazirine tetrafluoroborate has been reported previously.<sup>2</sup>

**Laser Flash Photolysis Experiments.** The computer-controlled nanosecond laser flash photolysis system employed in this study has been previously described.<sup>24</sup> The excitation source was the third harmonic of a Nd:YAG laser (355 nm, 20 mJ/pulse, < 8 ns/pulse). Sample cells for laser experiments were constructed of 7 × 7 mm<sup>2</sup> Suprasil quartz tubing. Each sample contained 2 mL of aerated HPLC grade solvent (except for N<sub>2</sub>-purged acetone) to which was added 20 μL of a diazirine stock solution (0.10–0.15 M of diazirine in acetonitrile). The final concentration of diazirine precursor was in the range of 1.0–1.5 mM, with absorption at the excitation wavelength of 355 nm in the 0.2–0.4 range. In the quenching experiments, small amounts (1 to 50 μL) of neat alkene were added to the sample cells in dichloromethane. Pyridine concentrations in the range of 0.047–0.10 M were used. Samples were shaken after every laser shot to ensure their homogeneity. All experiments were conducted at room temperature (22 ± 1 °C).

**Computational Method.** The geometries of the halo-(pyridinium)carbenes and alkenes used in this work were optimized with the Gaussian03 suite of programs.<sup>25</sup> Geometry optimizations were carried out at the B3LYP level with the 6-31G\* basis set. Frequency calculations were computed to ensure that each optimized structure corresponds to a minimum on the potential energy surface (no imaginary frequencies). TD-DFT calculations were carried out at the B3LYP/6-31G\* level, using the halo(pyridinium)carbenes optimized structures.

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**Supporting Information Available:** Cartesian coordinates and absolute energies for the halo(pyridinium)carbenes, as well as spin, spatial symmetry, excitation energy, and oscillator strength for the halo(pyridinium)carbenes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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