Generation and Reactivity of Simple Chloro(aryl)carbenes within the Cavities of Nonacidic Zeolites

Reinaldo Moya-Barrios and Frances L. Cozens*

Contribution from the Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada

Received July 5, 2006; E-mail: fcozens@dal.ca

Abstract: A number of *para*-substituted chloro(aryl)carbenes are generated within the cavities of a series of dry alkali metal cation-exchanged zeolites (LiY, NaY, KY, RbY, and CsY) upon laser flash photolysis of the corresponding diazirine precursor. The absolute reactivity of the chloro(aryl)carbene is found to be strongly dependent on both the nature of the electron-donating and -withdrawing properties of the aryl substituent and the nature of the zeolite charge-balancing cations. The results strongly suggest that two opposing mechanisms for capture of the carbene can occur depending on whether the zeolite framework behaves as a nucleophilic reagent or an electrophilic reagent in its reaction with the carbene center. Hammett relationships for the decay of the carbene as a function of aryl substituent and zeolite counterion versus the σ^+ substituent parameter support a change in mechanism as the carbene center toggles between being electron poor and electron rich. For the electron-poor chloro(4-nitrophenyl)carbene, a framework adduct is proposed upon reaction of the nucleophilic [Si−O−Al]$^-$ bridge with the carbene center, and for the electron-rich chloro(4-methoxyphenyl)carbene, an adduct with the tight Li$^+$ cation is proposed.

Introduction

Zeolites are well-known crystalline aluminosilicate materials with an open framework structure constructed of corner-linked [SiO$_4$]$^{4-}$ and [AlO$_4$]$^{5-}$ tetrahedra where every aluminum present in the framework results in a net negative charge, which must be charge-balanced by a cation.[1,2] The assembly of the tetrahedral units results in a variety of interesting topologies each involving a periodic array of molecular-sized pores, channels, or cavities. For the faujasite-type zeolites, the large void space associated with the 13 Å cavities is connected to four neighboring cavities in a tetrahedral array via 7.4 Å pores. This periodic arrangement of pores and cavities allows the efficient incorporation of many organic guest molecules within the interior spaces of the zeolite framework.

Because of the presence of the negative charge on the framework, which results from the tetracoordinated aluminum, and the positive charge of the charge-balancing cations, the zeolite framework can be considered amphoteric, possessing both Lewis basic and Lewis acidic sites. The strength of these acidic and basic sites can readily be manipulated by changing the nature of the charge-balancing cation, with Lewis base strength increasing and Lewis acid strength decreasing as the cation size becomes larger.[3−5]

Much of the data concerning the nature of Lewis acid and base sites within a range of zeolite types have been derived from spectroscopic studies, such as IR and NMR, of electron-

pair accepting or donating guest molecules located within the framework void space of these zeolites.[6−9] An additional and equally interesting method to investigate the interior properties of zeolites involves examining the reactivity of strongly electrophilic or nucleophilic species within these zeolite cavities. For example, zeolite encapsulated reactive carbocations are known to have much longer lifetimes and significantly reduced reactivity in Li$^+$-exchanged zeolites as compared to Cs$^+$-exchanged zeolites.[10,11] This reactivity trend nicely reflects the Lewis acid−base properties of the cation-exchanged zeolites, where Cs$^+$-zeolites are basic in nature and Li$^+$-zeolites are acidic in nature, and is consistent with the notion that electrophilic species are more reactive toward the [Si−O−Al]$^-$ active sites as the Lewis basicity of the zeolite increases upon going from LiY to CsY.[5,6,10−12]

The behavior of singlet carbenes within the cavities of zeolites[13,14] may also be of interest, because these reactive species can, in principle, display both electrophilic and nucleo-

(1) Breck, D. W. *Zeolite Molecular Sieves: Structure, Chemistry and Use*; John Wiley & Sons: New York, 1974.
(2) *Zeolite Chemistry and Catalysis*; Rabo, J. A., Ed.; ACS Monograph; American Chemical Society: Washington, DC, 1976.
(3) Huang, M.; Adnot, A.; Kaliaguine, S. *J. Catal.* **1992**, *137*, 322−332.
(4) Barthomeuf, D. *Catal. Rev.* **1996**, *52*, 521−612.
(5) Barthomeuf, D. *J. Phys. Chem.* **1984**, *88*, 42−45.

(6) Barthomeuf, D. In *Acidity and Basicity of Solids: Theory, Assessment, and Utility*; Fraissard, J., Petrakis, L., Eds.; Kluwer Academic Publishers: Netherlands, 1994; p 181−197.
(7) Ward, J. W. In *Zeolite Chemistry and Catalysis*; Rabo, J. A., Ed.; American Chemical Society: Washington, DC, 1976; p 118−284.
(8) Grey, C. P. In *Handbook of Zeolite Science and Technology*; Auerbach, S. M., Carrado, K. A., Dutta, P. K., Eds.; Marcel Dekker: New York, 2003; p 205−255.
(9) Pfeifer, H.; Ernst, H. *Annu. Rep. NMR Spectrosc.* **1994**, *28*, 91−187.
(10) O'Neill, M. A.; Cozens, F. L.; Schepp, N. P. *Tetrahedron* **2000**, *56*, 6969−6977.
(11) O'Neill, M. A.; Cozens, F. L.; Schepp, N. P. *J. Am. Chem. Soc.* **2000**, *122*, 6017−6027.
(12) Heidler, R.; Janssens, G. O. A.; Mortier, W. J.; Schoonheydt, R. A. *J. Phys. Chem.* **1996**, *100*, 19728−19734.
(13) Kupfer, R.; Brinker, U. H. *Liebigs Ann.* **1995**, 1721−1725.
(14) Kupfer, R.; Poliks, M. D.; Brinker, U. H. *J. Am. Chem. Soc.* **1994**, *116*, 7393−7398.
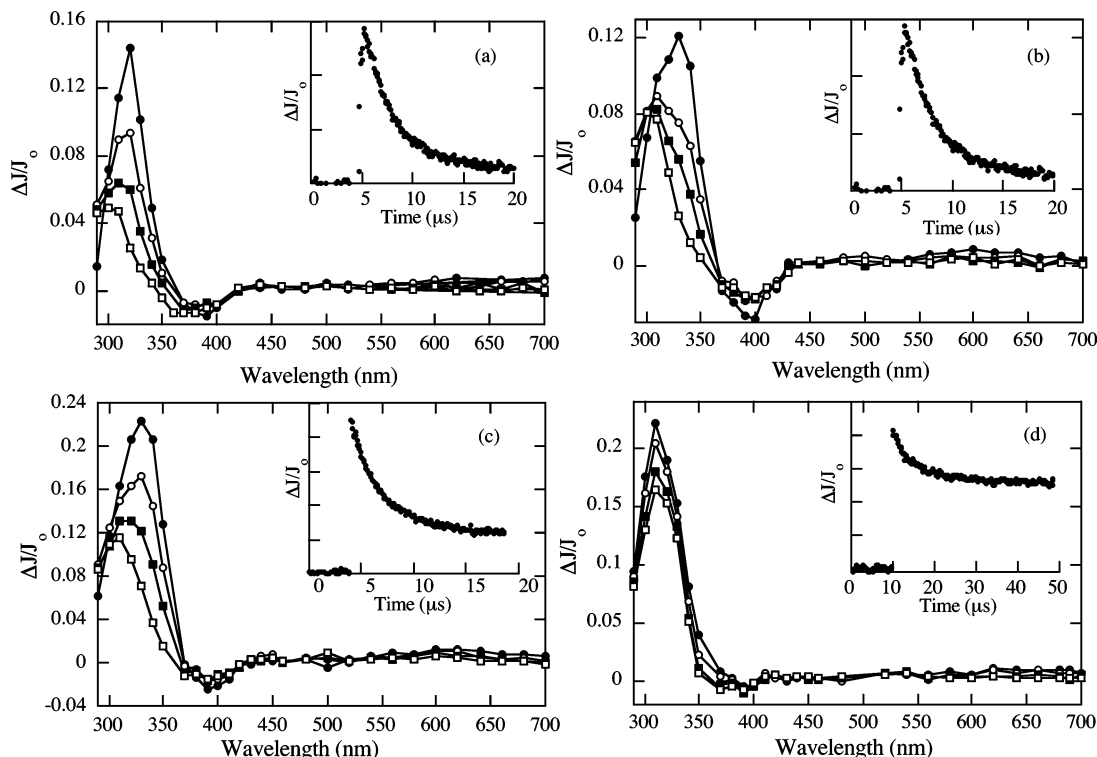
Figure 1. Transient diffuse reflectance spectra obtained upon 355 nm laser excitation of (a) 3-chloro-3-(phenyl)diazirine **1a** ($\langle s \rangle = 0.2$), (b) 3-chloro-3-(4-methylphenyl)diazirine **1b** ($\langle s \rangle = 0.5$), (c) (3-chloro-3-(4-chlorophenyl)diazirine) **1c** ($\langle s \rangle = 0.5$), and (d) 3-chloro-3-(4-trifluoromethylphenyl)diazirine **1d** ($\langle s \rangle = 0.5$) incorporated into the cavities of dry RbY. Insets show the transient decay kinetics at (a) 320 nm, (b) 330 nm, (c) 330 nm, and (d) 310 nm. All spectra were obtained under vacuum conditions, and the spectral windows were taken at (a) 1.5 μs (●), 2.7 μs (○), 4.2 μs (■), and 13.0 μs (□), (b) 1.40 μs (●), 2.44 μs (○), 3.80 μs (■), and 14.1 μs (□), (c) 1.40 μs (●), 2.52 μs (○), 4.36 μs (■), and 14.2 μs (□), and (d) 1.90 μs (●), 3.60 μs (○), 9.60 μs (■), and 34.3 μs (□) after laser irradiation.

philic character.[15] Thus, by examining the reactivity of a series of singlet carbenes within different zeolites, it ought to be possible to obtain information such as the relative importance of the Lewis acid and the Lewis base properties of zeolites in determining the chemistry of these incorporated guest molecules. In the present work, we have studied the reactivity of a variety of 4-substituted chloro(aryl)carbenes **2a–f** formed by laser irradiation of the appropriate diazirines **1a–f**, eq 1, and have examined the reactivity of these carbenes as a function of the aryl substituent and the composition of zeolite Y. Our results show that both variables not only have a distinct influence on the reactivity of the carbenes, but also on the mechanism of the reactions of the carbenes within the zeolite cavities.

(1)

a   X = H
b   X = CH$_3$
c   X = Cl
d   X = CF$_3$
e   X = OCH$_3$
f   X = NO$_2$
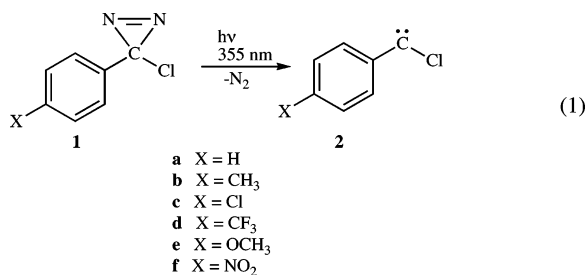
Results

Generation of Chloro(aryl)carbenes in Dry Alkali Metal Cation-Exchanged Zeolites. Chloro(phenyl)-, Chloro(4-methylphenyl)-, and Chloro(4-chlorophenyl)carbenes, 2a–2c. The diffuse reflectance spectra obtained upon laser irradiation of

diazirines **1a–1c** incorporated at loading levels (molecules of diazirine per supercage) of $\langle s \rangle = 0.2$–0.5 in RbY and CsY are dominated by short-lived transients with absorption maxima at 320 or 330 nm, as well as a long-lived absorption band near 310 nm and permanent bleaching between 360 and 430 nm, Figure 1a–c. The short-lived transients can be identified as the corresponding chloro(aryl)carbenes **2a–2c** on the basis of the following observations. In each case, the absorption maximum of the transient matches well with the known absorption maximum of the same carbene previously generated in solution.[16] In addition, the bleaching between 360 and 430 nm corresponds nicely with the absorption of the diazirines in this spectral region. Thus, the zeolite-incorporated diazirines are depleted upon laser irradiation, with the carbenes being the expected products upon photodecomposition of the diazirines.

The insets in Figure 1a–c show the time-resolved decays of carbenes **2a–2c** in RbY at room temperature. These decays, as well as those obtained in CsY, fit well to a simple, first-order rate expression. Rate constants, calculated by nonlinear least-squares fitting of the decay profiles to a single-exponential rate expression, are summarized in Table 1. The decays remained unchanged in the presence of oxygen, but were accelerated upon addition of methanol or 2-chloroacrylonitrile to the diazirine/zeolite composite. This behavior provides further evidence for the identification of the transients as the chloro(aryl)carbenes,

(15) Moss, R. A. In *Carbene Chemistry*; Bertrand, G., Ed.; Marcel Dekker: New York, 2002; p 57–101.
(16) Gould, I. R.; Turro, N. J.; Butcher, J., Jr.; Doubleday, C., Jr.; Hacker, N. P.; Lehr, G. F.; Moss, R. A.; Cox, D. P.; Guo, W.; Munjal, L. A.; Perez, L. A.; Fedorynski, M. *Tetrahedron* **1985**, *41*, 1587–1600.

Table 1. First-Order Rate Constants (k_{obs}) for the Decay of the Chloro(aryl)carbenes in the Alkali Metal Cation-Exchanged Y Zeolites under Dry Vacuum Conditions at 24 ± 1 °C

	k_{obs} (10^5 s^{-1})					
	4NO$_2$PhClC:	4CF$_3$PhClC:	4ClPhClC:	PhClC:	4CH$_3$PhClC:	4CH$_3$OPhClC:
zeolite	**2f**	**2d**	**2c**	**2a**	**2b**	**2e**
LiY	too fast	2.1 ± 0.2	too fast	too fast	too fast	too fast
NaY	too fast	0.65 ± 0.05	too fast	too fast	too fast	too fast
KY	too fast	0.84 ± 0.06	3.6 ± 0.4	5.2 ± 0.5	5.5 ± 0.5	too fast
RbY	too fast	1.6 ± 0.1	3.1 ± 0.3	3.6 ± 0.4	4.5 ± 0.4	too fast
CsY	too fast	too fast	3.4 ± 0.3	3.1 ± 0.3	3.9 ± 0.4	too fast

which, as singlet carbenes,[16] are known to be insensitive to oxygen and to be reactive toward alcohols and electron-poor alkenes.[16,17]

The long-lived absorption band at 300 nm observed upon laser irradiation of **1a**−**1c** does not match the absorption maxima of carbenes **2a**−**2c** and must be due to the formation of a different photogenerated species. In previous work,[18] this species was identified as α,α′-dichlorobenzaldazine produced by addition of chloro(phenyl)carbene **2a** to its diazirine precursor, eq 2 (Ar = Ph), which is a well-known reaction of carbenes generated from diazirines in solution.[19−21] This assignment is consistent with the absorption maximum near 300 nm for the azine in solution,[20] and with the isolation upon thermolysis of **1a** in CsY of 2,5-diphenyl-1,3,5-oxadiazole, which is produced by hydrolysis of the azine and subsequent cyclization, eq 2.[22]
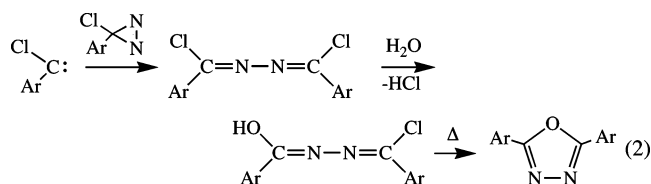
Because the absorption maxima of the long-lived absorption bands observed upon irradiation of **1b** and **1c** in RbY and CsY are similar to that for the azine generated upon irradiation of **1a**, it is reasonable to suggest that the corresponding substituted α,α′-dichlorobenzaldazines (eq 2, Ar = 4-CH$_3$Ph from **1b** and 4-ClPh from **1c**) are responsible, at least in part, for the absorption near 300 nm.

Results obtained upon laser irradiation of **1a**−**1c** in KY were somewhat similar to those in RbY and CsY, with the spectra showing absorption due to carbenes **2a**−**2c** near 320 nm, bleaching at 360−430 nm, and the long-lived absorption band at 300 nm. However, the absorption by the carbenes near 320 nm in this cation-exchanged zeolite was much weaker than that observed in RbY and CsY, and appeared as a small shoulder on the long-wavelength side of 300 nm bands instead of distinct maxima. The presence of substantial bleaching between 360 and 430 nm, but only weak carbene absorption, suggests that the carbenes decay with two distinct components in KY. One decay component corresponds to carbenes generated in an environment where they react sufficiently slowly to be observed. This time-resolved decay component fit well to a simple first-
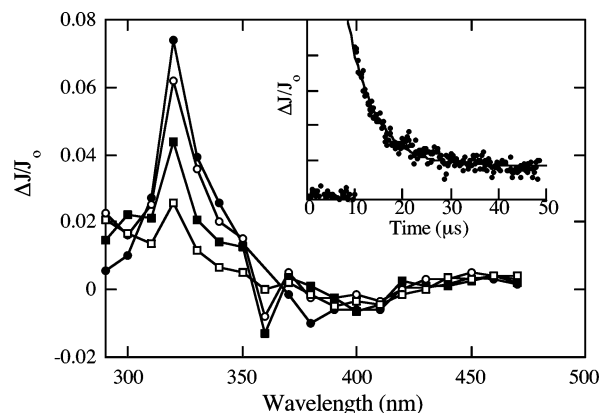

Figure 2. Transient diffuse reflectance spectra obtained upon 355 nm laser excitation of 3-chloro-3-(phenyl)diazirine **1a** ($\langle s \rangle = 0.5$) in LiY at −26 °C under dry vacuum conditions. The inset shows the decay kinetics at 320 nm. The spectral windows were taken at 1.48 μs (●), 3.60 μs (○), 5.12 μs (■), and 14.8 μs (□) after laser irradiation.

order rate expression, giving the rate constants summarized in Table 1. The other component comes from carbenes generated in a more reactive microenvironment, where the decay is too fast and therefore undetectable, and takes place within the time duration of the laser system with rate constants $>5 \times 10^6$ s^{-1}. The relatively small transient signal due to the carbene in KY indicates that the majority of the initially formed carbenes are too reactive to be directly observed within this cation-exchanged zeolite.

In NaY and LiY, only bleaching between 360 and 430 nm and the long-lived absorption at 300 nm were observed, with no direct spectral evidence for the presence of carbenes **2a**−**2c**. Because bleaching indicates that carbene formation had occurred upon irradiation, the inability to detect the carbenes suggests that they decay too rapidly within NaY and LiY to be observed. In previous work, the presence of carbene **2a** within NaY and LiY was established by detection of the 4,4′-bipyridine-**2a** ylide produced after laser irradiation of **1a** in NaY and LiY with co-incorporated 4,4′-bipyridine.[18] Similar results were obtained in the present work, whereby ylides with absorption maxima at 450 nm were observed from the reaction of 4,4′-bipyridine with carbenes **2b** and **2c** in NaY. Thus, it is reasonable to conclude that our inability to observe carbenes **2a**−**2c** resulted from these carbenes having short-lifetimes within the cavities of NaY and LiY.

In the present work, further information concerning the behavior of carbene **2a** in LiY was obtained by carrying out experiments at reduced temperatures. As shown in Figure 2, when laser irradiation of diazirine **1a** was carried out in LiY at a reduced temperature of −26 °C, an absorption band at 320 nm was observed that is closely similar to that for **2a** in

(17) Moss, R. A.; Turro, N. J. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, 1990; pp 213−238.
(18) Moya-Barrios, R.; Cozens, F. L. *Org. Lett.* **2004**, *6*, 881−884.
(19) Liu, M. T. H.; Toruyama, K. *J. Phys. Chem.* **1972**, *76*, 797−801.
(20) Bonneau, R.; Liu, M. T. H. *J. Phys. Chem. A* **2000**, *104*, 4115−4120.
(21) Rosenberg, M. G.; Brinker, U. H. *J. Org. Chem.* **2003**, *68*, 4819−4832.
(22) Cronin, J.; Hegarty, A. F.; Cashell, P. A.; Scott, F. L. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1708−1719.
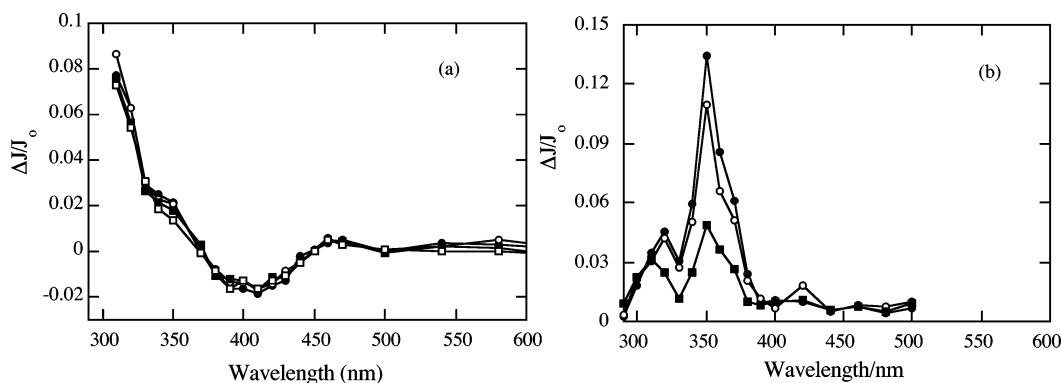
Figure 3. Transient diffuse reflectance spectra obtained upon 355 nm laser excitation of 3-chloro-3-(4-methoxyphenyl)diazirine **1e** ($\langle s \rangle = 0.5$) in (a) RbY at 24 ± 1 °C and (b) CsY at -28 ± 1 °C. All spectra were obtained under dry vacuum conditions, and the spectral windows were taken at (a) 1.56 μs (●), 3.20 μs (○), 5.48 μs (■), and 15.4 μs (□) and (b) 3.08 μs (●), 4.52 μs (○), and 14.1 μs (■) after laser irradiation.

solution[16] and in RbY and CsY. At this reduced temperature, the carbene decayed in a simple first-order manner, Figure 2 (inset), with a rate constant of 1.8×10^5 s^{-1} that is similar to the rate constant for the decay of **2a** in CsY at room temperature. As the sample temperature was increased, the observed rate constant for the decay of the carbene at 320 nm increased, and near 0 °C, the absorption at 320 nm was no longer present, with the carbene becoming too reactive to be observed. These results clearly indicate that carbene **2a** is considerably more reactive in LiY than in zeolites RbY and CsY where the carbene is readily detectable at room temperature.

Chloro(4-trifluoromethylphenyl)carbene 2d. Laser flash photolysis of 3-chloro-3-(4-trifluoromethylphenyl)diazirine **1d** incorporated into dry RbY under evacuated conditions was dominated by bleaching between 360 and 430 nm and a strong absorption band centered at 310 nm, Figure 1d. Within 20 μs after the laser pulse, the 310 nm absorption band partially decayed with a first-order rate constant of 1.6×10^5 s^{-1}, leaving a long-lived absorption centered at 310 nm. The chloro(4-trifluoromethylphenyl)carbene **2d** is known to have a strong absorption band at approximately 300 nm.[16] Thus, the time-resolved diffuse reflectance spectra in Figure 1d show that carbene **2d** is generated upon laser irradiation of the diazirine precursor, and then decays to reveal a long-lived species at 310 nm, which is likely the carbene-diazirine adduct (eq 2, Ar = 4-CF$_3$Ph) similar to that previously described for carbene **2a**. Upon the addition of methanol to the diazirine/zeolite sample, the rate constant for the decay at 310 nm steadily increased, while the long-lived component continued to show no decay over the time scale of the experiment. This provides further evidence that the two components of the absorption at 310 nm are due to two distinct species and is consistent with the assignment of the short-lived component of the 310 nm absorption as the carbene **2d**.

Unlike carbenes **2a**−**2c** that were readily detectable in both RbY and CsY, the 4-CF$_3$-substituted carbene **2d** was not directly observed in CsY. In this zeolite, only the long-lived component of the band at 310 nm and bleaching between 360 and 430 nm due to photodecomposition of the diazirine precursor were observed, suggesting that the carbene decays too rapidly to be detected in CsY. This contrary behavior of **2d** continued in zeolites with the smaller alkali metal cations such that absorption due to **2d** remained strong in KY and continued to be readily observed in both NaY and LiY. In addition, as shown in Table 1, the rate constants for the first-order decay of **2d** decreased

upon going from CsY to NaY, which is opposite from the trends observed with carbenes **2a**−**2c** whose reactivities increase upon going from CsY to NaY.

Chloro(4-methoxyphenyl)carbene 2e. Figure 3a shows the transient diffuse reflectance spectra obtained upon laser irradiation of 3-chloro-3-(4-methoxyphenyl)diazirine **1e** in dry RbY under vacuum conditions at room temperature. Long-lived absorption in the 310 nm region and bleaching between 370 and 460 nm due to photodecomposition of the diazirine are observed, but no absorption near 340 nm, the known absorption maximum of the chloro(4-methoxyphenyl)carbene **2e**,[16] is evident in these spectra. Identical results were obtained upon laser irradiation in CsY and KY, with only long-lived absorption at 310 nm and bleaching between 370 and 460 nm being observed and no absorption near 340 nm.

At -28 °C, laser irradiation of diazirine **1e** in CsY did lead to the formation of an absorption band at 350 nm that corresponds well with carbene **2e**, Figure 3b. As the temperature increased, the rate constant for the decay of **2e** increased, and near 0 °C, carbene **2e** decayed too rapidly to be observed. In addition, the transient diffuse reflectance spectrum generated upon 355-nm laser irradiation of diazirine **1e** co-incorporated in CsY with 4,4′-bipyridine at room temperature is dominated by a large broad absorption band centered at 540 nm. The position of the absorption maximum at 540 nm and the shape of the band are closely similar to the absorption spectrum of the 4,4′-bipyridine-carbene **2e** ylide in solution.[23] Together, the low-temperature and 4,4-bipyridine results indicate that carbene **2e** is photogenerated in CsY at room temperature and is sufficiently long-lived to undergo a rapid reaction with co-incorporated 4,4′-bipyridine to form the corresponding 4,4′-bipyridine-carbene **2e** ylide, but is too short-lived to be directly observed on the microsecond time scale.

In LiY and NaY, laser irradiation at room temperature of diazirine **1e** produced the transient spectra shown in Figure 4, which consist of two absorption bands, one centered at 320 nm that showed little decay on the time scale of the laser system, and an additional intense broad absorption band located at 370 nm that decayed slowly within these zeolites with a rate constant in LiY of 1.1×10^4 s^{-1} under evacuated conditions. The static absorption at 320 nm is likely the carbene−diazirine adduct similar to that previously described for the reaction of the other

(23) In hexanes, reaction of chloro(4-methoxyphenyl)carbene and 4,4′-bipyridine produces the corresponding carbene ylide at 490 nm.
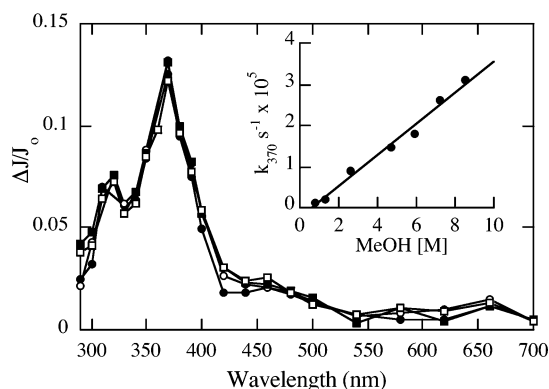
Figure 4. Transient diffuse reflectance spectra obtained upon 355 nm laser excitation of 3-chloro-3-(4-methoxyphenyl)diazirine **1e** ($\langle s \rangle = 0.5$) in LiY under dry vacuum conditions. The spectral windows were taken at 1.56 μs (●), 3.20 μs (○), 5.48 μs (■), and 15.4 μs (□) after laser irradiation. The inset shows the relationship between the rate constant for the decay of the 370 nm absorption and increasing methanol concentration within LiY.

carbenes with their diazirine precursors, eq 2 (Ar = 4-CH$_3$OPh). The 370 nm absorption, which decays slowly on the time scale of the experiment, is located at a longer wavelength and is much broader in shape as compared to the known absorption properties of the chloro(4-methoxyphenyl)carbene **2e**, which in solution has a sharp absorption band with a maximum at 340 nm.[16] These results therefore indicate that the carbene **2e** is not observable within LiY and NaY and that the 370 nm absorption is due to a different transient species formed upon the photolysis of diazirine **1e** within these two Lewis acidic zeolites.

At −28 °C, the transient diffuse spectrum in LiY was identical to that obtained at room temperature and was again characterized by strong absorption bands at 320 and 370 nm, with no absorption at 350 nm due to carbene **2e**. However, laser irradiation at room temperature of **1e** in LiY or NaY with co-incorporated 4,4-dipyridine at room temperature did result in the formation of the 4,4′-bipyridine−**2e** ylide at 540 nm. Thus, carbene **2e** was indeed generated within these zeolites, but even at a reduced temperature of −28 °C decayed too rapidly to be observed.

The decay of the transient with absorption at 370 nm in LiY and NaY was not affected by the addition of oxygen to the sample. The rate constant for the decay did, however, increase in the presence of methanol. The decay rate constant of the 370 nm band increased in a linear manner with respect to methanol concentration, and linear least-squares analysis gave a bimolecular rate constant for quenching of the transient at 370 nm with methanol of $k_q = 5.1 \times 10^5$ M^{-1} s^{-1}, Figure 4, inset.

Chloro(4-nitrophenyl)carbene 2f. Laser experiments with 3-chloro-3-(4-nitrophenyl)diazirine **1f** incorporated in all of the alkali-metal cation-exchanged Y zeolites under dry vacuum conditions yielded transient diffuse reflectance spectra dominated by an absorption maximum centered at approximately 420 nm, Figure 5a. In CsY, RbY, and KY, this absorption band was very strong and did not decay even on the longest time scale of our laser system ($k < 1 \times 10^3$ s^{-1}). In NaY and LiY, the absorption at 420 nm was less intense, and the transient decay was faster with first-order observed rate constants of 2.3×10^4 and 3.4×10^4 s^{-1}, respectively. The introduction of oxygen had no effect on the absorption or the rate constant of the transient observed at 420 nm in any of the alkali metal cation-exchanged Y zeolites.

The possibility that the transient observed at 420 nm is the chloro(4-nitrophenyl)carbene **2f** can be discounted because this carbene presents a very different absorption spectrum in hydrocarbon solution with an absorption maximum at 320 nm.[24] In addition, the lifetime of **2f** in solution is only a few hundreds nanoseconds, while the transient observed at 420 nm is persistent on all time scales of our laser system in CsY, RbY, and KY, and decays only slowly in NaY and LiY.

Carbene **2f** has previously been shown to react with acetone to produce a ylide with a strong absorption band at 590 nm.[25] As shown in Figure 5b, vapor inclusion of acetone in RbY rapidly quenched the intensity of the signal at 420 nm and produced a new absorption band centered at approximately 600 nm, consistent with the formation of the acetone−**2f** ylide.[25] This band was quenched by the inclusion of oxygen, which is in agreement with the known reactivity of the carbene−acetone ylide in solution.[25] The formation of this ylide leads to the conclusion that carbene **2f** is generated in the zeolites and can be trapped by acetone, but decays with a rate constant that is too rapid for the carbene to be observed.

Product Studies. Thermolysis at 80 °C for 48 h of the unsubstituted 3-chloro-3-(phenyl)diazirine **1a** incorporated with a loading level $\langle s \rangle = 0.5$ in NaY under dry nitrogen conditions led to the formation of benzaldehyde (95% of isolated material after extraction) and 2,5-diphenyl-1,3,4-oxadiazole (5%) as the major products. As mentioned above, the oxadiazole is likely generated by addition of carbene **2a** to its diazirine precursor to form the α,α′-dichlorobenzaldazine,[19−21] followed by hydrolysis and cyclization.[22] Benzaldehyde is the expected product from direct addition of water to the carbene; however, as described below, benzaldehyde may also be generated by hydrolysis of a carbene-framework complex.

Thermolysis of NaY samples containing 3-chloro-3-(aryl)-diazirines **1b−1e** yielded only the corresponding arylaldehydes with no detectable trace of 2,5-diaryl-1,3,4-oxadiazoles upon GC analysis of the extracted material. Given that the laser irradiation of **1b−1e** led to formation of the absorption band at 300−310 nm assigned, at least in part, to the corresponding substituted α,α′-dichlorobenzaldazines, the absence of the oxadiazoles was surprising. It is, however, possible that the oxadiazoles were produced, but due to the additional substituents on the aryl ring were too large to be effectively extracted from the zeolite samples.

Thermolysis of 3-chloro-3-(4-nitrophenyl)diazirine **1f** at 80 °C for 48 h under argon followed by continuous extraction with dichloromethane as described above for the diazirines **1a−1e** yielded no GC-detectable products. However, addition of 4 mL of methanol to the zeolite sample after the thermolysis at 80 °C was complete, followed by extraction of the zeolite−methanol slurry with dichloromethane, led to the detection of 4-nitrobenzaldehyde (89%) and 4-nitrobenzaldehyde dimethyl acetal (11%). Thermolysis (80 °C, 48 h) of a NaY sample containing the product 4-nitrobenzaldehyde under argon, followed by the addition of 4 mL of methanol and extraction with dichloromethane in the same manner as above, afforded exclusively unreacted *p*-nitrobenzaldehyde, and no 4-nitrobenzaldehyde dimethyl acetal was obtained under these conditions.

(24) Bonneau, R.; Liu, M. T. H. *J. Chem. Soc., Chem. Commun.* **1989**, 510−512.
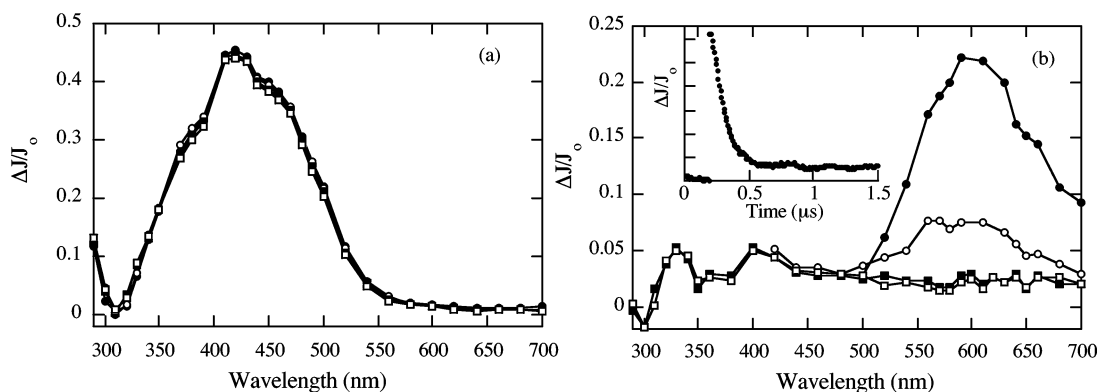(25) Bonneau, R.; Liu, M. T. H. *J. Am. Chem. Soc.* **1990**, *112*, 744−747.

Figure 5. Transient diffuse reflectance spectra obtained upon 355 nm laser excitation of 3-chloro-3-(4-nitrophenyl)diazirine **1f** ($\langle s \rangle$ = 0.2) (a) in RbY under dry vacuum conditions and (b) in RbY upon vapor inclusion of acetone. Inset shows the decay trace monitored at 600 nm. The spectral windows were taken at (a) 2.04 μs (●), 3.20 μs (○), 6.84 μs (■), and 14.9 μs (□), and (b) 240 ns (●), 500 ns (○), 3.42 μs (■), and 7.46 μs (□) after laser irradiation.
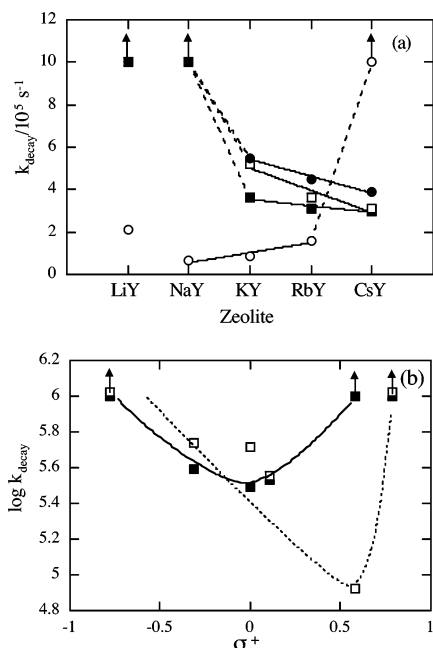

Figure 6. (a) Effect of zeolite composition on the rate constant for the decay of the (□) chloro(phenyl)carbene **2a**, (●) chloro(4-methylphenyl)-carbene **2b**, (■) chloro(4-chlorophenyl)carbene **2c**, and (○) chloro(4-trifluoromethylphenyl)carbene **2d** at 24 ± 1 °C. (b) Relationship between the rate constant for the decay of chloro(aryl)carbenes **2a**–**2f** and σ^+ substituent parameters in (■) CsY and (□) KY at 24 ± 1 °C. Curves were drawn to highlight curvature and do not represent lines of best fit. Data points with arrows represent lower limit estimates of the decay rate constants.

These results suggest that, in NaY, 4-nitrobenzaldehyde dimethyl acetal is not produced by a reaction between methanol and 4-nitrobenzaldehyde within NaY.

Discussion

From the rate constant data presented in Table 1, several trends are evident with regards to the effect of carbene structure and zeolite composition on the rate constants for the decays of the chloro(aryl)carbenes **2a**–**2f**. Two of these trends are illustrated in Figure 6a, which shows the rate constants for the decay of carbenes **2a**–**2d** as a function of zeolite composition. As can be seen for carbenes **2a**–**2c**, the rate constants increase slightly as the zeolite composition changes from CsY to KY, and then dramatically increase in NaY and LiY. Conversely, the reactivity of carbene **2d** shows the opposite trend, with the rate constant decreasing significantly upon going from CsY to

RbY, followed by a more gradual decrease from RbY to NaY, and then a slight increase in LiY. Thus, carbenes **2a**–**2c** are more reactive in the more strongly Lewis acidic (i.e., electrophilic) zeolites LiY and NaY and less reactive in the more strongly Lewis basic (i.e., nucleophilic) zeolites RbY and CsY, while carbene **2d** is less reactive in the electrophilic zeolites and more reactive in the nucleophilic zeolites.

A reasonable explanation for the two opposing trends in Figure 6a is that carbenes **2a**–**2c**, which do not contain strongly electron-withdrawing aryl substituents, are displaying nucleophilic character, while carbene **2d**, which contains a strongly electron-withdrawing CF$_3$ group, is behaving as an electrophile. In other words, the mechanism of the reaction of the carbenes within the zeolite cavities changes as a function of substituent, with carbenes **2a**–**2c** attacking an available electrophile within the zeolite cavity, and carbene **2d** reacting with an available nucleophile.

The effect of substituents is more clearly illustrated in Figure 6b, which shows the relationship between the rate constant for decay of the carbenes as a function of the Hammett substituent parameter σ^+ in CsY and KY. The plot includes data for carbenes **2e** (4-CH$_3$O) and **2f** (4-NO$_2$), which could not be observed and react within all of the cation-exchanged Y zeolites with rate constants $>10^6$ s^{-1}. As can be seen, the data for the reaction in CsY are clearly curved, with a negative slope for the carbenes containing electron-donating substituents, and a positive slope for carbenes with electron-withdrawing substituents. This behavior is consistent with the known ambiphilic nature of chloro(aryl)carbenes[26,27] and is typical for a change in mechanism whereby the ambiphilic carbenes switch from behaving as nucleophiles (negative slope) to electrophiles (positive slope). In the more strongly electrophilic KY, the data are also curved, but the change in slope is only evident with the strongly electron-withdrawing 4-NO$_2$ group.

While curved Hammett plots have been previously observed for other ambiphilic carbenes,[28] Hammett plots of reactions of chloro(aryl)carbenes with quenchers are typically linear with little evidence of curvature. As a result, it is reasonable to suggest that the behavior of the chloro(aryl)carbenes in the present work is due to the unusual properties of the zeolite

(26) Soundararajan, N.; Platz, M. S.; Jackson, J. E.; Doyle, M. P.; Oon, S. M.; Liu, M. T. H.; Anand, S. M. *J. Am. Chem. Soc.* **1988**, *110*, 7143–7152.
(27) Moss, R. A.; Fan, H.; Hadel, L. M.; Shen, S.; Wlostowska, J.; Wlostowski, M.; Kroghjespersen, K. *Tetrahedron Lett.* **1987**, *28*, 4779–4782.
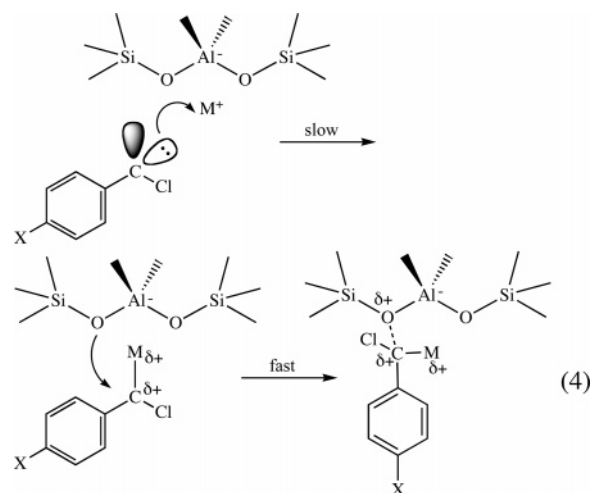(28) Moss, R. A.; Perez, L. A. *Tetrahedron Lett.* **1983**, *24*, 2719–2722.

cavities. One of these properties is the availability of both nucleophilic and electrophilic sites within the zeolite framework that allow the ambiphilic nature of the chloro(aryl)carbenes to be fully expressed in a single environment. Previous work has demonstrated that the oxygen atom of $[Si-O-Al]^-$ bridges is nucleophilic, with the nucleophilicity of the oxygen increasing as the alkali metal cation is changed from Li^+ to Cs^+.[5,6] This framework nucleophile can react with electron-deficient species such as carbocations to generate framework bound alkoxy species.[11,29,30] A similar reaction can occur between the framework $[Si-O-Al]^-$ active sites and the electrophilic carbenes **2d** and **2f**, which in this case would lead to the formation of framework bound ylide-like intermediates, as shown in eq 3.


(3)
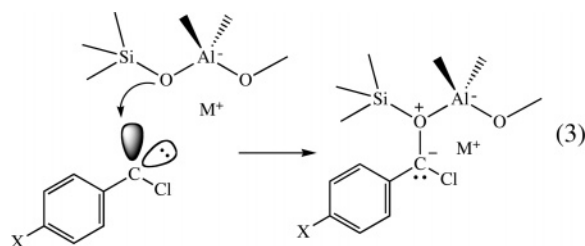
In addition, it is well known that the alkali metal cations, especially Li^+ and Na^+, interact with lone-pair electrons of guest molecules such as pyridine and pyrrole and that these cations have strong Lewis acid properties in Y zeolites and can act as effective electrophiles.[6,31,32] Furthermore, results from studies in solution have shown that carbenes are reactive toward metal cations. In particular, fluoro(phenyl)carbene and chloro(fluoro)-carbene react rapidly ($k \approx 10^7-10^8$ M^{-1} s^{-1}) with Li^+ in acetonitrile to generate α-halo lithium carbenoids.[33,34] In addition, stable carbene–alkali metal complexes have been isolated where the carbenic center is coordinated directly to either Li^+, Na^+, or K^+.[35,36] Thus, a reasonable mechanism for the reaction of the more electron-rich carbenes within the Y zeolites is rate-determining addition of the carbene to the alkali metal cation to generate an α-chloro-metal cation complex, eq 4. This complex is likely to be unstable, especially for weakly coordinating cations such as Rb^+ and Cs^+, and would presumably react further with the zeolite framework to generate a framework bound carbenoid-like structure, eq 4.

An alternative possibility that cannot be entirely discounted at the present time is that, instead of the zeolites providing nucleophilic and electrophilic sites for the reaction with the carbenes, they modulate the properties of an additional quencher that may be present within the zeolite. In particular, despite all attempts to ensure that water is excluded from the zeolites during sample preparation, we can only be confident that the zeolite samples prepared in the present work contain less than 1% water, which may still be sufficient to act as the primary reagent for

(29) Mota, C. J.; Esteves, P. M.; de Amorim, M. B. *J. Phys. Chem.* **1996**, *100*, 12418−12423.
(30) Kramer, G. J.; van Santen, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 2887−2897.
(31) Yashima, T.; Hara, N. *J. Catal.* **1972**, *27*, 329−341.
(32) Ward, J. W. *J. Colloid Interface Sci.* **1968**, *28*, 269−280.
(33) Moss, R. A.; Fan, H.; Gurumurthy, R.; Ho, G.-J. *J. Am. Chem. Soc.* **1991**, *113*, 1435−1437.
(34) Tippmann, E.; Platz, M. S. *J. Phys. Chem. A* **2003**, *107*, 8547−8551.
(35) Alder, R. W.; Blake, M. E.; Bortolotti, C.; Bufali, S.; Butts, C. P.; Linehan, E.; Oliva, J. M.; Orpen, A. G.; Quayle, M. J. *Chem. Commun.* **1999**, 241−242.
(36) Arduengo, A. J., III; Tamm, M.; Calabrese, J. C.; Davidson, F.; Marshall, W. J. *Chem. Lett.* **1999**, 1021−1022.

(4)

reaction with the carbenes. In CsY and RbY, the incorporated water is only loosely bound to the framework, as illustrated in Scheme 1a. As a result, water in CsY and RbY will be substantially more nucleophilic than that in LiY or NaY, and more electrophilic carbenes will become increasingly longer-lived as the alkali-metal cation is changed from Cs^+ to Li^+. On the other hand, in LiY and NaY, the oxygen of water interacts strongly with the smaller metal cations. This weakens the nucleophilicity of the incorporated water, but can increase its acidity, thus providing an electrophilic proton to react with the more nucleophilic carbenes, Scheme 1b.

Scheme 1

(a) $X = NO_2$, CF_3 (b) $X = CH_3O$, CH_3, H, Cl
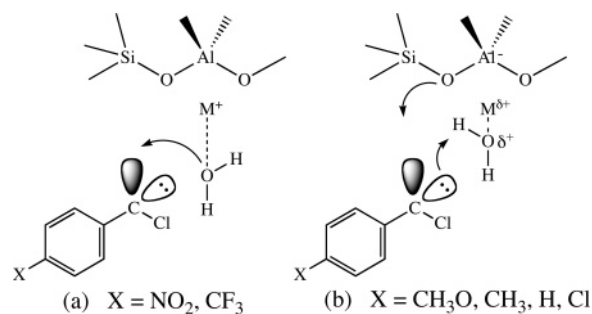
Because both possible sets of mechanisms described above highlight the ability of the zeolite framework to provide both a nucleophilic and an electrophilic environment, it is difficult to determine which one is more prevalent, or whether both are contributing to the observed trends. Furthermore, results from the product studies do not provide clear evidence for one particular mechanism. The results, which showed that the arylaldehydes are the major products, are consistent with water adding directly to the carbenic center; however, both of the carbene-framework complexes in eqs 3 and 4 are likely to be prone to hydrolysis, presumably by slow reaction with trace amounts of intrazeolite water, which would ultimately give the arylaldehydes as the final products.

Nucleophilic addition of the framework to carbene **2f** to generate a carbene-framework bound complex rather than addition of water is suggested by the formation of 4-nitrobenz-aldehyde dimethyl acetal upon irradiation of **1f** in NaY. This product was isolated only when methanol was added to the zeolite sample after thermolysis was complete. Because the chloro(4-nitrophenyl)carbene decays rapidly within 100 ns, and

methanol was only added after several hours of thermolysis, the dimethyl acetal cannot be a product from the direct reaction of the carbene with methanol. On the other hand, a framework bound complex may be sufficiently long-lived to still be available for reaction after thermolysis is complete and would then upon addition of methanol be readily converted to the observed product as shown in eq 5.
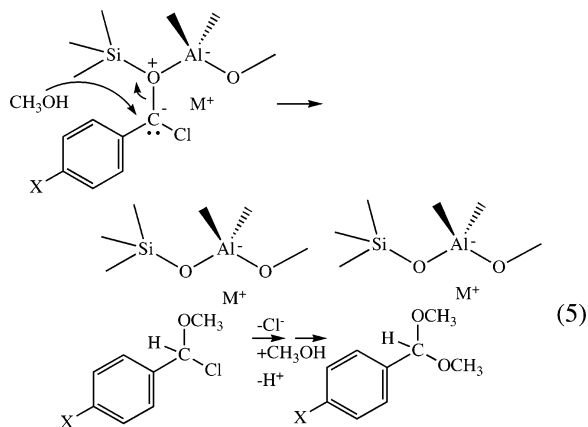
Also of interest is the observation that, while the chloro(4-nitrophenyl)carbene was not directly observed, a transient at 420 nm was generated after irradiation of **1f** in all of the Y zeolites, Figure 5a. Species with absorption maxima in this region have previously been observed upon the addition of nucleophiles to this carbene. In particular, the reaction of carbene **2f** with ethyl acetate[37] and tetrahydrofuran[38] generates ylides with absorption maxima at 490 nm, while the reaction with oxygen produces the carbonyl oxide at 400 nm.[39] In addition, the 4-nitrophenyldichloromethide carbanion was recently generated by addition of chloride to **2f**, and it has a maximum at 420 nm.[40] Thus, while a definitive assignment of the 420 nm band is not possible, its spectral properties are consistent with the formation of the framework-**2f** ylide shown in eq 3 (X = NO_2).

The long-lived species with absorption at 370 nm generated upon laser irradiation of 3-chloro-3-(4-methoxyphenyl)diazirine **1e** in NaY and LiY, Figure 4, is also noteworthy, because it has properties that are typically observed for benzylic carbocations, especially 4-methoxybenzylic cations. In particular, the 4-methoxyphenethyl cation has an absorption maximum near 340 nm,[41] which is in the same region as the 370 nm absorption maximum for the transient from **1e**. In addition, the 370 nm band was reactive toward methanol, as expected for an electrophilic species such as the carbene–metal cation complex. Furthermore, the 370 nm band is only observed in LiY and NaY, which is consistent with the expectation that only Li$^+$ and Na$^+$ would form a strong enough bond with the carbene to generate a transient carbocation with a lifetime sufficiently long to be observed.

An additional feature of the trends shown in Figure 6a is that the nucleophilic behavior of carbenes **2a–2c**, as well as

(37) Chateauneuf, J. E.; Liu, M. T. H. *J. Am. Chem. Soc.* **1991**, *113*, 6585–6588.
(38) Celebi, S.; Tsao, M.-L.; Platz, M. S. *J. Phys. Chem. A* **2001**, *105*, 1158–1162.
(39) Liu, M. T. H.; Bonneau, R.; Jefford, C. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1482–1483.
(40) Moss, R. A.; Tian, J. *Org. Lett.* **2006**, *8*, 1245–1247.
(41) Cozens, F. L.; Kanagasabapathy, V. M.; McClelland, R. A.; Steenken, S. *Can. J. Chem.* **1999**, *77*, 2069–2082.

the 4-CH_3O carbene **2e**, is not limited to the highly electrophilic LiY and NaY zeolites, but appears to continue in the less electrophilic and more nucleophilic CsY and RbY zeolites. Similarly, the electrophilic 4-NO_2 carbene **2f** is too reactive to be observed both in the more nucleophilic CsY and RbY zeolites as well as in the less nucleophilic NaY and LiY zeolites. Thus, while changing the substituents from electron-donating to electron-withdrawing causes a change in the carbene's selectivity toward the different kinds of reactive sites in the zeolites, the reaction of each of the individual carbenes **2a–2c**, **2e**, and **2f** remains unchanged upon going from the more electrophilic LiY to the more nucleophilic CsY.

The situation appears to be somewhat different for the CF_3-containing carbene **2d** whose reactivity decreases upon going from CsY to NaY, but then increases slightly in LiY. This may indicate that **2d** reacts as an electrophile in zeolites that possess the stronger nucleophiles, while in a weakly nucleophilic, but strongly electrophilic zeolite like LiY, the carbene adds as a nucleophile to the zeolites framework.

Conclusions

While the precise mechanism of the reaction of the carbenes within the Y zeolites cannot be unambiguously determined, the results described above clearly indicate that the Y zeolite framework can provide both a nucleophilic and an electrophilic environment for reactions of potentially ambiphilic materials such as the chloro(aryl)carbenes studied in the present work. One consequence of this amphoteric behavior is that these Y zeolites are not likely to be suitable media for capturing and stabilizing carbenes, at least not simple singlet carbenes. For example, our results suggest that adding strongly electron-donating substituents to a normally electrophilic carbene in an attempt to capture the carbene within a zeolite cavity is not likely to be a successful strategy: the zeolite will instead reveal its electrophilic character and rapidly react with the electron-rich carbene. Whether or not this is valid even for strongly stabilized carbenes, such as diamino carbenes that are stable in solution, has not yet been determined.

Experimental Section

Materials. The 3-chloro-3-(aryl)diazirines **1a–1f** were prepared following the Graham reaction.[42] All diazirines were characterized by ^{1}H and ^{13}C NMR spectroscopy (Bruker 500 MHz) using CDCl$_3$ as the solvent. Spectroscopic grade acetone and 4,4′-bipyridine (Aldrich) were used as received. Spectroscopic grade solvents (<0.02% water) used in zeolite sample preparation were commercially available (OmniSolv, BDH) and were used without additional purification. Methanol was doubly distilled prior to use.

NaY (Si/Al = 2.4) was purchased from Aldrich and used as received. The alkali metal cation Y zeolites were prepared by stirring ~5 g of NaY with 3 M aqueous solutions of the corresponding chloride salts (LiCl, KCl, RbCl, CsCl) at 80 °C for 1 h in Nanopure water. The zeolites were then filtrated and washed with Nanopure water until no more chlorides appeared in the filtrate. The presence of chlorides was tested using a saturated silver nitrate solution. This procedure was repeated three times, and the zeolite was calcinated between exchanges. NaY has three types of exchangeable cations. The number of cations per unit cell of zeolite Y are 16 site I cations, 32 site II cations, and 8 site III cations. Only site II and site III cations are accessible to guest

(42) Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396–4397.

molecules.[43] The degree of cation exchange in Y zeolites is typically 47% for LiY, 97% for KY, 44% for RbY, and 47% for CsY. For larger cations such as Rb^+ and Cs^+, only the Na^+ that occupy type II and type III sites can be readily exchanged.[44] Hydrated Li^+ does not readily exchange the type I cations, which results in a lower percent exchange.

Preparation of Diazirine–Zeolite Samples. Diazirines used in this work were incorporated within the zeolite samples by the following general procedure. The hydrated zeolite was heated for at least 24 h in an oven at 450 °C to remove the adsorbed water. The zeolite was removed from the oven and poured into a flamed-dry test tube. Rapidly, to prevent the absorption of water from the atmosphere, 20 mL of hexanes (HPLC grade) was added, and the test tube was covered with a septum. A certain volume (typically < 100 μL) of a concentrated (typically 0.1–1 M) hexanes or dichloromethane stock solution containing diazirine was added to the zeolite, suspended in hexanes. The zeolite–hexanes slurry was stirred for 3 h at room temperature. After this time, the test tube was centrifuged, the supernatant layer was decanted, and another 20 mL of hexanes was added to the zeolite to remove any compound on the zeolite surface. The slurry was stirred for at least 10 min, centrifuged, and the supernatant liquid separated from the zeolite. The supernatant layer was kept to determine the actual loading level of the zeolite sample.

The hexanes-saturated zeolite was placed in a desiccator under vacuum overnight to eliminate most of the hexanes presented in the sample. The zeolite–adsorbate composite was transferred from the desiccator to a 3 × 7 mm^2 quartz cell for laser experiments. This part of the procedure was conducted in a glovebag under dry nitrogen to avoid the absorption of water vapor from the air. After the zeolite–adsorbate composite was transferred to the laser cell, it was connected to a vacuum line equipped with a diffusion pump (10^{-4} mmHg) and left overnight to ensure the complete removal of any remaining hexanes and oxygen from the zeolite sample.

Analysis of the hexanes washing decants by UV–visible spectroscopy was used to determine the loading level, $\langle s \rangle$ (defined as molecules of diazirine per zeolite supercage), of organic guest molecules included within the zeolite sample. The absorbance of decants was compared to calibration curves of the different substrates, and the occupancy level of the sample was determined.

Preparation of zeolite samples containing diazirine and 4,4′-bipyridine was carried out in a manner similar to the one described above, by incorporating the two molecules separately. The diazirine was incorporated first, followed by 4,4′-bipyridine.

Addition of methanol, acetone, and alkenes for the quenching plots was conducted after diazirine incorporation and evacuation. The laser cells containing the diazirine–zeolite composites were preweighed. In this manner, the mass of the zeolite–diazirine samples could be accurately determined. The typical zeolite mass used for the laser experiments was approximately 300–400 mg. To add the coadsorbed carbene quencher, the laser cells were sealed with a rubber septum. Next, a small amount of the quencher (typically 1–2 μL) was injected into the top of the cell using a syringe. Care was taken to prevent the contact of the zeolite powder with the liquid. The sample cell was then gently heated with hot air to vaporize the quencher molecule, during which time the cell was rotated to ensure even distribution. Special care was taken to prevent the heating of the part of the laser cell where the diazirine–zeolite composite was deposited. The sample was then allowed to cool and was thoroughly shaken before the laser experiments were carried out.

Product Studies. 3-Chloro-3-(aryl)diazirines were thermally decomposed within the Y zeolites, and the products obtained were extracted from the zeolite and analyzed. The procedure followed is herein described. A sample of the appropriate zeolite of approximately 2 g containing the diazirine to be studied was placed in a test-tube sealed with a rubber septum and under UHP nitrogen or argon. The sample was stirred and heated at 80 °C (using an oil bath and a temperature controller) for 48 h. After thermolysis, 20 mL of dichloromethane was added to the zeolite, and the resulting slurry was stirred for 24 h. The slurry was centrifuged and the supernatant liquid collected. The zeolite was washed with an additional 20 mL of dichloromethane and centrifuged. The liquid was decanted and transferred to the previous extract. Product distribution and identification were accomplished by GC/FID and GC/MS by comparison with authentic reference samples.

Nanosecond Laser Flash Photolysis. The computer-controlled nanosecond laser flash photolysis system was employed in this study and has been previously described.[11] The excitation source was the third harmonic of a Spectra Physics Nd:YAG laser (355 nm, ≤20 mJ/pulse, <8 ns/pulse). Diffuse reflectance experiments involve measuring the fraction of reflected light absorbed by the transient, denoted as the reflectance change, $\Delta J / J_o$, where J_o is the reflectance intensity before laser excitation and ΔJ is the change in reflectance intensity after excitation due to absorption by photogenerated transients. The diffuse reflected light is focused through a grating monochromator into a photomultiplier system before being captured with a Tektronix 620A digitizing oscilloscope and transferred via a GPIB interface to a Power Macintosh 7100 computer, which controls the laser system using a program written with LabView 3.0 software.

(43) Ramamurthy, V.; Turro, N. J. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1995**, *21*, 239–282.
(44) Van Bekkum, H.; Flanigen, E. M.; Janson, J. C. *Introduction to Zeolite Science and Practice*; Elsevier Science Ltd.: Amsterdam, 1991.