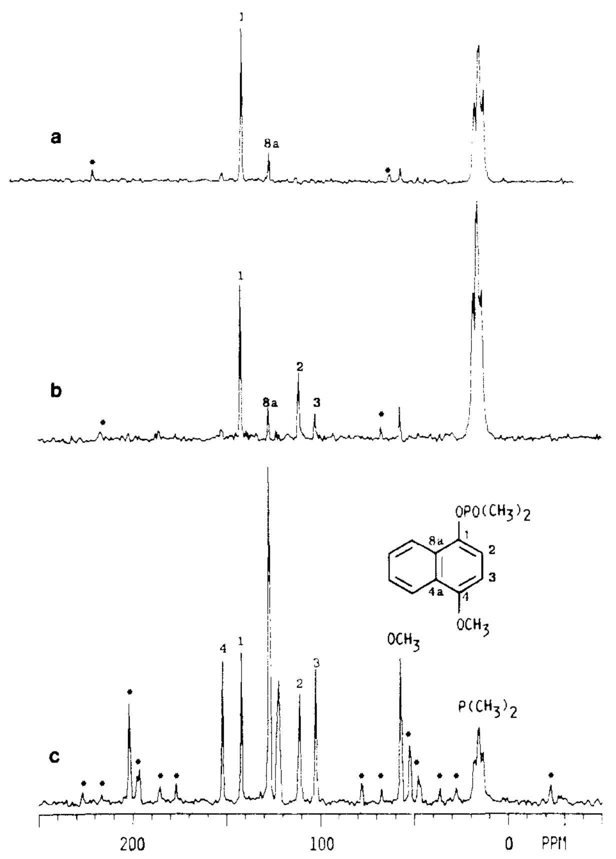

Figure 2. ^{1}H–^{13}C–^{31}P DCP/MAS ^{13}C NMR spectra (2a,b) and ^{1}H–^{13}C CP/MAS ^{13}C NMR spectrum (2c) of (4-methoxy-1-naphthyl)dimethylphosphinate, **2**. Assignments are indicated on the spectra; * identifies spinning sidebands (MAS = 4 ± 0.05 KHz). The dipolar dephased DCP spectrum, 2a, was generated by using a 40 μs dephasing interval.

from the ^{31}P atom, appears in the long contact time spectrum, Figure 1a.

Figure 2 (parts a–c) depicts spectra of (4-methoxy-1-naphthyl)dimethylphosphinate, **2**. Figure 2c is the conventional ^{1}H–^{13}C CP/MAS ^{13}C NMR spectrum, with assignments. Figure 2b, the DCP spectrum, reveals all aromatic carbons two- and three-bonds distant from the ^{31}P atom. The strong two-bond interaction, $r_{P-C(1)} = 0.267$ nm, yields the intense resonance at 145 ppm (note the signal discrimination between the two oxygenated aromatic carbons). The X-ray crystal structure of **2** reveals that the phosphorus atom lies roughly in the plane defined by the aromatic carbons and trans to the bridgehead carbon.[4] This conformation maximizes the difference in the three bond internuclear distances, $r_{P-C(2)} = 0.313$ nm and $r_{P-C(8a)} = 0.391$ nm, and is reflected in the relative intensities, i.e., cross polarization rates, of the resonances of these centers.[5] One of three aromatic carbons four-bonds removed from the phosphorus atom, C(3), is represented in the spectrum but is too distant (0.454 nm) to account for the observed intensity in the spectrum. The X-ray data reveal an intermolecular ^{31}P–^{13}C(3) contact at a comparable internuclear distance, 0.482 nm. In fact, the C(3) intensity in the spectrum is the sum of both inter- and intramolecular contributions.

A DCP signal from the methoxyl carbon of **2** is evident in Figure 2b. This signal, as intense as that from C(8a), arises entirely from a ^{13}C–^{31}P intermolecular interaction developed over the uncharacteristically short internuclear distance of 0.387 nm. Hence, weak DCP resonances from intermolecular ^{31}P–^{13}C cross polarization are observed and can be comparable in strength to signals which arise from intramolecular interactions across three bonds. With this caveat in mind, the ^{1}H–^{13}C–^{31}P DCP/MAS ^{13}C NMR experiment is principally an intramolecular probe. Figure 2a depicts the application of the dipolar dephasing technique[6] in editing the DCP spectrum of **2**. This spectrum retains solely the nonprotonated C(1) and C(8a) resonances in the aromatic region.

The elucidation of the carbon bonding network around phosphorus centers in solids by ^{1}H–^{13}C–^{31}P DCP/MAS ^{13}C NMR is a new capability that has broad potential for applications in structure determination and reaction site identification in phosphorus derivatized solids.

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(4) Hagaman, E. W.; Brown, G. M., unpublished results.

(5) For ^{13}C–^{31}P cross polarization contact times $\ll T_{CP}$, the ratio of integrated signal intensities and the ratio of rates, $(T_{CP})^{-1}$, are equivalent. In the present case, with contact time $< T_{CP}$, the argument is qualitatively but not rigorously correct.

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Pyridine Ylide Formation by Capture of Phenylchlorocarbene and *tert*-Butylchlorocarbene. Reaction Rates of an Alkylchlorocarbene by Laser Flash Photolysis

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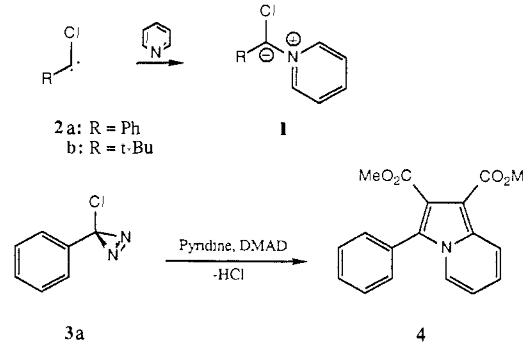
Fluorenylidene and the naphthylcarbenes are intercepted by acetone or acetonitrile to give ylides which are easily detected by *l*aser *f*lash *p*hotolysis (LFP).[1] Phenylchlorocarbene does not react at a measurable rate with these quenchers to form ylides[2] although its *p*-Cl, *p*-CF$_3$, and *p*-nitro derivatives react with acetone to form carbonyl ylides.[3] We herein report that phenylchlorocarbene (**2a**) and *tert*-butylchlorocarbene (**2b**) react with pyridine to give ylides **1a,b** which serve as ideal kinetic probes of carbene dynamics. This permits measurements of the first absolute rate constants of an "invisible" alkylchlorocarbene, which lacks a suitable chromophore for its direct detection.[4]



2a: R = Ph
b: R = t-Bu

1

3a

4

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(1) (a) Barcus, R. L.; Hadel, L. M.; Johnston, L. J.; Platz, M. S.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3928. (b) Griller, D.; Hadel, L. M.; Nazran, A. S.; Platz, M. S.; Wong, P. C.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 2227.

(2) Soundararajan, N.; Jackson, J. E.; Platz, M. S., unpublished research at Ohio State University.

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(4) A similar strategy of ylide trapping has been used to monitor the dynamics of methylene. (a) Turro, N. J.; Cha, Y.; Gould, I. R. *J. Am. Chem. Soc.* **1987**, *109*, 2101. (b) Turro, N. J.; Cha, Y.; Gould, I. R.; Padwa, A.; Gasdaska, J. R.; Tomas, M. *J. Org. Chem.* **1985**, *50*, 4417.

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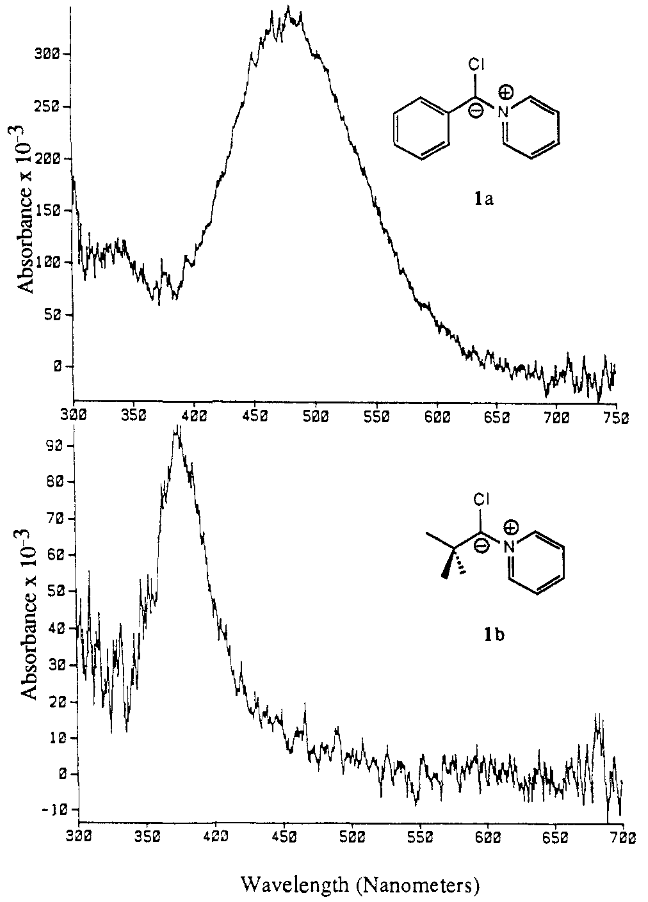

Figure 1. Transient optical density spectra of ylides **1a** and **1b**. These were obtained by using an EG&G Princeton Applied Research Corp. *O*ptical *M*ultichannel *A*nalyser (OMA). Data were collected during 1.0 (**1a**) and 0.3 (**1b**) μs windows, beginning ca. 4.5 (**1a**) and 0.5 (**1b**) μs after the 10 ns, 351 nm laser pulse which generated the carbene. Both species were observed in 10% pyridine in toluene.

LFP of diazirines[5] **3a,b** in the presence of pyridine produces the transient spectra shown in Figure 1. These transients are not present in the absence of pyridine and are attributed to ylides **1a,b**. The rates of formation of **1a,b** are first order in [pyridine] with absolute rate constants of 3.35 ± 0.29 × 10^8 M^{-1} s^{-1} and 2.38 ± 0.18 × 10^9 M^{-1} s^{-1} for reaction of phenylchlorocarbene (**2a**) and *tert*-butylchlorocarbene (**2b**), respectively. Photolysis of phenylchlorodiazirine (**3a**) in the presence of both pyridine and dimethylacetylenedicarboxylate (DMAD) produces product **4**[6] in ~30% yield by dipolar cycloaddition of DMAD to the ylide, followed by loss of HCl. The absolute rate constant for reaction of ylide **1a** with DMAD was determined by LFP and found to be 1.57 ± 0.06 × 10^6 M^{-1} s^{-1} in toluene at 25 °C.[7]

Pyridinium ylides **1a,b** are ideal probes of the dynamics of carbenes **2a,b** because they are intensely absorbant (λ_{max} 480 and 376 nm, respectively, Figure 1) and long lived (τ > 100 μs and ~5 μs, respectively).[8] The addition of a carbene quencher such as tetramethylethylene (TME) or 1-hexene (HEX) increases the apparent rate of formation of **1a** and decreases its yield as expected. Analysis of the effect of olefin concentration on the rate and extent of ylide formation in the usual manner (see below) yields the rate constants for reaction of phenylchlorocarbene given in Table I. The data obtained agree within experimental error by analysis of either carbene **2a** or ylide **1a**, which confirms the spectral assignments and mechanistic hypotheses. The error limits are somewhat greater for the indirect methods but are still acceptable.

Table I. Absolute Rate Constants for Reaction of Phenylchlorocarbene (**2a**) with Olefins in Toluene at 25 °C

	species	rate constants[a] (M^{-1} s^{-1})[a]	
λ (nm)	monitored	direct analysis[c]	Stern–Volmer Analysis[d]
318[b]	**2a**	1.31 ± 0.10 × 10^8 (TME)	*e*
318[b]	**2a**	1.10 ± 0.05 × 10^6 (HEX)	*e*
480	**1a**	1.27 ± 0.22 × 10^8 (TME)	0.95 ± 0.18 × 10^8 (TME)
480	**1a**	1.14 ± 0.16 × 10^6 (HEX)	0.95 ± 0.16 × 10^6 (HEX)

[a] ± two standard deviations. [b] LFP analysis of carbene decay in the absence of pyridine, data of ref 9. [c] Obtained from a plot of k_{obsd} versus [olefin], ref 10. [d] Obtained from a plot of (maximum OD of **1a**)$^{-1}$ versus [olefin], ref 10. [e] Not applicable.

Table II. Absolute Rate Constants for Reaction of *tert*-Butylchlorocarbene (**2b**) with Olefins in Toluene at 25 °C

	species	rate constants (M^{-1} s^{-1})	
λ (nm)	monitored	direct analysis	Stern–Volmer analysis
380	**1b**	4.28 ± 0.82 × 10^7 (T3H)	5.25 ± 0.52 × 10^7 (T3H)
380	**1b**	1.05 ± 0.07 × 10^7 (BVE)	0.99 ± 0.13 × 10^7 (BVE)

The kinetics of *tert*-butylchlorocarbene (**2b**) cannot be studied directly due to the absence in the carbene of a useable UV–vis chromophore. However, a plot of the observed pseudo-first-order rate constant for growth of pyridinium ylide **1b** against [pyridine] is linear and yields the absolute rate constant for the reaction of **2b** with pyridine (2.38 ± 0.18 × 10^9 M^{-1} s^{-1}). The intercept of this plot yields k_0 which is the sum of all first-order and pseudo-first-order decay processes of **2b** in the absence of pyridine or olefin.[10] The carbene lifetime $\tau = 1/k_0$ in the absence of quenchers is ~90 ns and is controlled by reaction of the carbene with solvent, impurities, and diazirine precursor and by intramolecular rearrangement (k_1).[4b] Utilization of pyridinium ylide **1b** as demonstrated for **1a** allows measurement of the absolute rate constants for reactions of this "invisible" carbene with *trans*-3-hexene (T3H) and *n*-butyl vinyl ether (BVE) (Table II). We have also observed pyridinium ylides of two other "invisible" carbenes (benzylchlorocarbene[11] and adamantylidene)[12] as well as ylides derived from pyrazine, thiophene, quinoline, and thioanisole. Finally, in combination with product studies, this pyridine probe technique presents a new strategy for the measurement of the absolute rates of intramolecular rearrangements of alkyl chloro and other "invisible" carbenes. These results will be published in due course, along with studies to determine the rate constants and activation parameters for 1,3-C–H insertion and 1,2-methyl migration, the intramolecular decay processes (k_1) in carbene **1b**.

Acknowledgment. Support of this work by the NSF is greatly appreciated.

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(6) The ylide–DMAD adduct **4** (heavy oil) was purified by preparative TLC: ^{1}H NMR ($CDCl_3$) AM 250 (250 MHz) δ 8.00–8.24 (m, 4 H) δ 7.24 (s, 5 H), δ 3.89 (s, 3 H), δ 3.78 (s, 3 H); IR (neat) 1730, 1710, 1690 cm^{-1}; *m/e* $C_{18}H_{15}NC_4$ calcd 309.1000, found 309.2000; major fragments at *m/e* 309, 278, 251, 191, 96, 78.

(7) Details of experimental procedures and apparatus are reported in ref 9.

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(10) The probe kinetics method was invented by J. C. Scaiano, see Chatgilialoglu et al. (Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5124) for an example and leading references.

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