The ability of the crude 5-LO-containing homogenate to convert arachidonic acid to 5-HETE decreased in a time-dependent manner on aerobic preincubation of the homogenate with 5,6-DHA. For an experiment using preincubation with 0.5 μM 5,6-DHA at 10 °C, a plot of preincubation time vs. the log of the fraction of original activity remaining was linear, with the half-life being ca. 12 min. Similar measurements of 5,12-DIHETE formation showed falloff parallel to that for 5-HETE as a function of preincubation with 5,6-DHA. These results, even though obtained with a crude enzyme preparation, clearly indicate time-dependent, irreversible inhibition of the leukotriene pathway by 5,6-DHA. This initial study is being extended in several pertinent directions. It is interesting that 5,8,11,14-eicosatetraynoic acid has been found not to inhibit the conversion of arachidonate to 5-HETE in human leukocytes.[14,15]

Registry No. 1, 58688-54-3; **2**, 80738-23-4; **2** methyl ester, 80764-50-7; **3**, 80764-51-8; **4**, 80764-52-9; **5**, 80764-53-0; **6**, 80764-54-1; **7**, 80738-22-3; **7** methyl ester, 80764-55-2; **8**, 80764-56-3; **9**, 80764-57-4; 3 (*Z*)-nonenal, 31823-43-5; methyl 4-formylbutyrate, 6026-86-4; arachidonic acid, 506-32-1.

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(14) Dr. Pierre Borgeat, unpublished results.

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Temperature Dependence of the Cycloaddition of Phenylchlorocarbene to Alkenes. Observation of "Negative Activation Energies"

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Chemists employ an extremely useful and effective model of activation energy as a barrier that must be overcome during the course of a reaction.[1] The barrier is usually positive in the energy sense, i.e., the energy of activation is higher than the energy of the reactants or the products. However, the activation energy, E_a, is merely a quantity associated with the slope of an experimental plot of log k_{obsd} vs. $1/T$ (Arrhenius plot). The magnitude of E_{obsd} may be positive, negative, or zero, depending on the complexity of the reaction being investigated.[2] When E_{obsd} is negative, a standard interpretation of the observation is available: the reaction under investigation is multistep and involves at least one intermediate that possesses at least two channels for reaction.[3-7]

Recently, small negative enthalpies of activation have been reported for the quenching of singlet fluorenylidene by several alkenes; the values were considered "statistically indistinguishable from zero".[8a] This report is one of the few dealing with measurements of absolute rate constants for carbene–alkene addition *in solution*. The others involve the additions to alkenes of diarylcarbenes,[8b] fluorenylidene,[8c] and phenylchlorocarbene (PhCCl).[9a] We have now determined activation parameters for the additions of PhCCl to several alkenes and report here results consistent with the occurrence of a dissociable intermediate in the carbene cycloaddition.

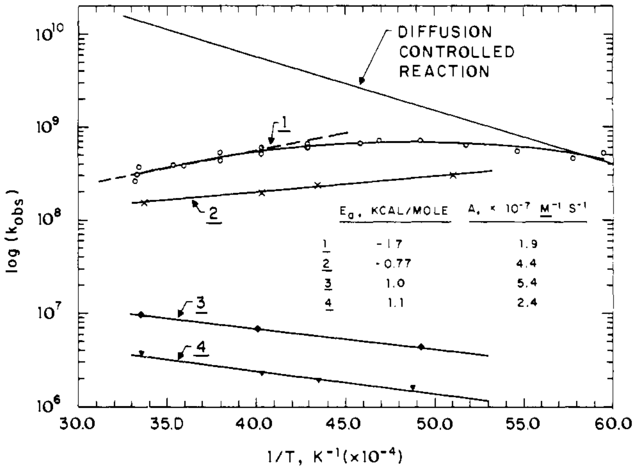

Figure 1. Arrhenius plot of the temperature dependence of the reaction of phenylchlorocarbene with olefins. Diffusion-controlled rate constants were calculated from the temperature dependence of the solvent viscosity.[11] The dashed line indicates results calculated between 301 and 248 K. Linear-regression coefficients for a second-order polynomial fit of all the data for **1** are $a_0 = 5.37$, $a_1 = 1436$, and $a_2 = -1.48 \times 10^5$.

The methods and system for the generation and monitoring of singlet PhCCl at various temperatures were similar to that described earlier.[9a] However, significant improvements were made to the laser flash photolysis apparatus previously employed to obtain the absolute rate constants for the addition of singlet PhCCl to olefins **1**–**4**.[9a] Specifically, we added a high-intensity pulsed

$Me_2C{=}CMe_2$ **1** $Me_2C{=}CHMe$ **2** *t*-$MeCH{=}CHEt$ **3**

$CH_2{=}CH$-*n*-Bu **4**

Xe lamp as the detection source, a newer, more sensitive monochromator, and a multiple-pulse delay unit to control the timing of the Xe lamp and the laser. Our new results, obtained with a different transient absorption system, differ significantly from the earlier results.[9a] The new rate constants are all higher by factors of 2–3. We attribute this to the systematic changes in the flash photolytic apparatus described above. As an independent check, Dr. J. C. Scaiano[9c] graciously determined k_{abs} for the addition of PhCCl to tetramethylethylene (**1**) on his laser flash system. The result, $k = 2.0 \times 10^8$ M^{-1} s^{-1}, is close to the average (2.3×10^8 M^{-1} s^{-1}) of our original[9a] and new (below) values. Clearly, the absolute rate constants are system dependent, and the accuracy of any given k_{abs} is low. However, it is the *precision* of the rate constant measurements that is important in examining temperature effects. In our case, the precision of the data points is ≤5%, and the reproducibility of the derived rate constants is ≤10%, so we can have reasonable confidence in the Arrhenius studies presented below.

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(9) (a) Turro, N. J.; Butcher, J. A.; Moss, R. A.; Guo, W.; Munjal, R. C.; Fedorynski, M. *J. Am. Chem. Soc.* **1980**, *102*, 7576. (b) The previous results[9a] were obtained with $\lambda_{ex} = 249$ nm, $\lambda_{obsd} = 320$ nm with a band-pass of 15 nm. Reexamination of the absorption spectrum of PhCCl in isooctane at room temperature showed a maximum at 308 nm (5-nm intervals, 4-nm band-pass), in excellent agreement with the spectrum recorded at 77 K in 3-methylpentane (See ref 9a). (c) National Research Council, Ottawa, Canada.

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Table I. Relative Rates vs. Temperature from Competition Experiments or from Absolute Rate Constants

olefin	$k_{\text{rel}}^{\text{comp}}$ (25 °C)^a	$k_{\text{rel}}^{\text{abs}}$ (25 °C)^{b,c}	$k_{\text{rel}}^{\text{comp}}$ (−42 °C)^{b,d}	$k_{\text{rel}}^{\text{abs}}$ (−42 °C)^{b,c}
1	1.0	1.0	1.0	1.0
2	0.62	0.48	0.33	0.37
3	0.028	0.030	0.0059	0.0084
4	0.011	0.012	0.0019	0.0031

[a] See ref 9a. [b] This work. [c] Relative rate constants were derived from absolute rate constants; errors ±10%. [d] Relative rate constants were determined by competition experiments in neat alkenes, with product analysis by reversed-phase (C_{18}) HPLC; error, ±2%.

PhCCl was generated by laser flash photolysis of phenylchlorodiazirine in isooctane solution (λ_{ex} = 351 nm). The transient absorption of PhCCl was monitored over 90% of decay at 310 nm with a bandpass of 4 nm[9b] as a function of time after the laser pulse in the presence of varying concentrations of the four olefinic quenchers, **1**–**4**. On average, 21 decays were monitored for each case. The second-order rate constants obtained for the addition of PhCCl to these olefins at 25 °C are (**1**) $(3.3 \pm 0.2) \times 10^8$ M^{-1} s^{-1}, (**2**) $(1.6 \pm 0.1) \times 10^8$ M^{-1} s^{-1}, (**3**) $(1.0 \pm 0.1) \times 10^7$ M^{-1} s^{-1}, and (**4**) $(3.8 \pm 0.2) \times 10^6$ M^{-1} s^{-1}. The local precision of the data is excellent, exceeding that obtained with the earlier experimental apparatus.[9a] Examination of the decay kinetics as a function of temperature leads to the results shown in Figure 1, where the apparent second-order rate constants are obtained from pseudo-first-order rate constants by using the expression $k_{\text{obsd}} = k/[\text{olefin}]$, where k is the pseudo-first-order rate constant.

The salient features of our results are as follows: (a) The Arrhenius plot for **1** shows pronounced curvature. As the temperature *decreases* from 301 to 213 K, k_{obsd} *increases* from $(2.7 \pm 0.1) \times 10^8$ M^{-1} s^{-1} to $(7.2 \pm 0.3) \times 10^8$ M^{-1} s^{-1}. The value of E_a^{obsd} is computed to be −1.7 ± 0.5 kcal/mol (Figure 1). At temperatures below 213 K, k_{obsd} decreases and E_a^{obsd} approaches the value for diffusion-controlled reaction. (b) The Arrhenius plot for **2** shows a small slope corresponding to an E_a^{obsd} of −0.77 ± 0.5 kcal/mol. (c) For **3** and **4**, a normal, positive activation energy of 1 ± 0.5 kcal/mol is evaluated from the Arrhenius plots.

As a check of the kinetic data, the relative rates for cycloaddition of PhCCl to alkenes **1**–**4** were measured at 25 and −42 °C by competitive techniques employing product analysis. Agreement between the relative determination by measurement of absolute rate constants via flash spectroscopy and by competitive methods via product analysis is acceptable (Table I).

These results can be interpreted in terms of a kinetic model for the reaction of PhCCl and an alkene, A, which is represented by the steps shown in eq 1 and 2, where PhCCl/A is a reversibly formed dissociable intermediate. If cyclopropane formation proceeds via eq 1 and 2, then k_{obsd} is not a single rate constant[10] but is related to the rate constants in eq 1 and 2 by eq 3 and 4.

$$\text{A} + \text{PhCCl} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{PhCCl/A} \tag{1}$$

$$\text{PhCCl/A} \xrightarrow{k_2} \text{cyclopropane} \tag{2}$$

$$k_{\text{obsd}} = k_1 k_2/(k_{-1} + k_2) \tag{3}$$

$$k_{-1}/k_2 = (k_1 - k_{\text{obsd}})/k_{\text{obsd}} \tag{4}$$

Since k_1 in eq 1 corresponds to normal diffusion, we can equate k_1 with k_{dif}, the rate constant for diffusion in isooctane. The temperature dependence of k_{dif} was computed from knowledge of the temperature dependence of solvent viscosity.[11] Thus, plots of log (k_{-1}/k_2) vs. $1/T$ may be constructed from our experimental data with the substitution of k_{dif} for k_1 in eq 4. The results are shown in Figure 2. Although no "new" information is supplied by this manipulation, the data are recast into a form that is both mechanistically relevant and easily related to the problems of carbenic selectivity.[12]

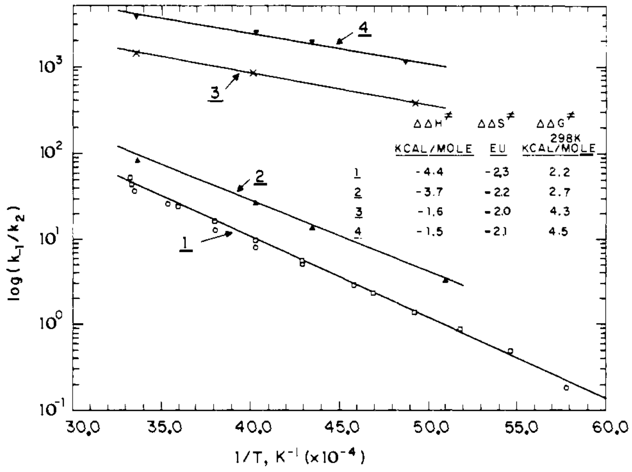

Figure 2. Arrhenius plots of the relative rates of dissociation and product formation from PhCCl/A according to eq 4. $\Delta\Delta G^{\ddagger}$ is calculated at 298 K. The datum at 168 K is excluded from this analysis, because it deviates substantially from the straight line. The freezing point of isooctane is 166 K. The error limits are ±0.5 kcal/mol.

The structure of the PhCCl/A intermediate, however, is not revealed by the kinetics. A structure that is consistent with the data and with current ideas concerning the reactions of singlet carbenes with alkenes[12] is one in which the vacant p orbital of the singlet carbene interacts with the π electrons of the alkene, resulting in the formation of a loose charge-transfer complex, which then has the option of collapsing to the cyclopropane product or of dissociating back to the starting materials. It appears that the more reactive alkenes have transition states leading to the complex that are looser with respect to the two components than do the less reactive olefins, as suggested more than a decade ago[13] to explain the temperature dependencies of the relative rate constants for alkene additions of Cl_2C. The kinetics are, however, also consistent with the structure of PhCCl/A as simply a "proximity pair" of reactants in a solvent cage.[10]

From the plot of log (k_{-1}/k_2) vs. $1/T$ (Figure 2), values of $\Delta\Delta G^{\ddagger}$, $\Delta\Delta H^{\ddagger}$, and $\Delta\Delta S^{\ddagger}$ may be computed for the competition between dissociation and completion of cycloaddition. The data in Figure 2 suggest that the differences in rates for the reactions of PhCCl with alkenes at any given temperature (as reflected by $\Delta\Delta G^{\ddagger}$) is due to changes in the relative enthalpies for cyclopropanation vs. dissociation.

Although the additions of PhCCl to alkenes **1**–**4** are entropy dominated (as is the case for fluorenylidene[8a]), the activation entropies are comparable (∼−20 eu) for each substrate, so that the observed rate constants depend upon the relative enthalpies for cyclopropanation vs. dissociation of the complexes. This de facto enthalpic control is expressed in larger k_{obsd} values for cyclopropanations of the more highly substituted alkenes (i.e., **1** > **2** > **3** > **4**), in accord with well-known features of carbene/alkene addition reactions.[12] Finally, it has been suggested that less reactive carbenes may react with alkenes via $\Delta H^{\ddagger}$-dominated transition states.[13] Experiments are in progress to test this idea.

In conclusion, the reaction of PhCCl and alkenes probably proceeds via weakly bound intermediate complexes whose structures are of the charge-transfer type. The competition in partitioning of the intermediates between cyclopropane formation or reversion to singlet PhCCl and olefin determines the observed rate constants and their temperature dependence.

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During the course of refereeing of this manuscript, a report of the reaction of triplet fluorenylidene with olefins demonstrated that "negative activation energies" also occur in some of these systems. The effect was attributed to reversible formation of *triplet* carbene–alkene complexes that are precursors to the final products.[14]

Acknowledgment. We thank the National Science Foundation for its generous support of this work. We also thank Dr. I. R. Gould for his assistance in extending the initial data points employed to generate Figures 1 and 2 and Dr. J. C. Scaiano for an independent determination of k_{abs} for the reaction of PhCCl and **1**. The authors thank Professor Cheves Walling for his thoughtful comments and suggestions.

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Synthesis and Structural Investigation of (Mesityl(diphenylmethylene)phosphine)bis(triphenylphosphine)platinum(0)

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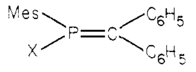
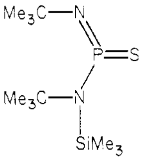
Mesityl(diphenylmethylene)phosphine (**1**)[1] is one of the few



1, X = lone pair
2, X = Cr(CO)$_5$
Mes = mesityl

known thermally stable phosphaalkenes with an essentially localized P=C double bond. The chemistry of this new class of compounds is just beginning to be developed.[2] It has been shown that **1** can act as an η^1 (σ P or "end-on") ligand toward metal centers,[3,4] as illustrated by the pentacarbonylchromium(0) complex **2**.[3]

It was of interest to investigate if the P=C function was also suited for η^2 (π or "side-on") coordination. For this purpose, Pt(0) is particularly favorable as it is known to undergo η^2 coordination not only with C=C bonds but also with a great variety of heteroalkenes, e.g., with the C=S bond of CS_2[5] or of sulfines,[6] the N=S bond of sulfinylanilines,[7] the P=S bond of the metathiophosphoric acid derivative **3**,[8] and even the P=P bond of the phosphorobenzene derivative **4**.[9]



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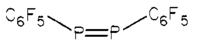

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Table I. ^{31}P NMR Spectrum (101.26 MHz) of 5

	δ^a	$^1J_{PtP}{}^b$	$^2J_{PP}{}^b$
P1	21.94	3359	P1P2, 29.6
P2	22.23	3392	P2P3, 11.1
P3	−33.48	505	P3P1, 56.4

[a] In ppm relative to external 85% H_3PO_4; toluene-d_{18}; −56.5 °C. [b] In Hertz.

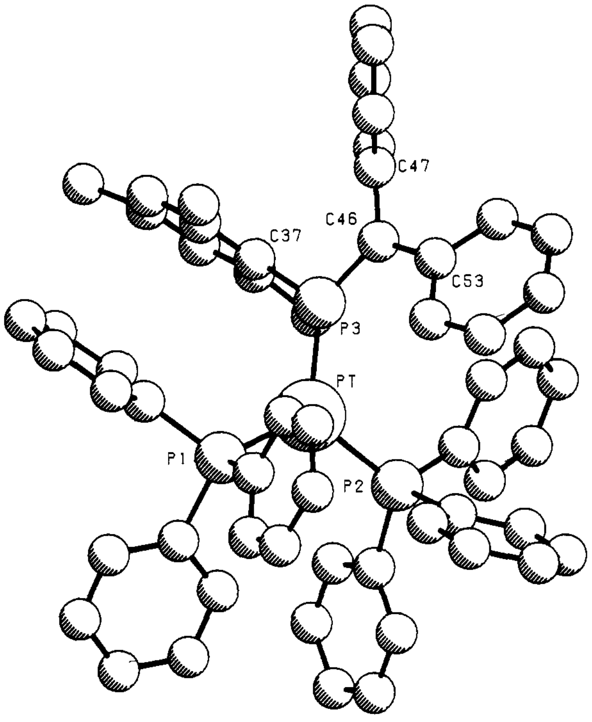

Figure 1. Structure of (mesityl(diphenylmethylene)phosphine)bis(triphenylphosphine)platinum(0).

We now report the synthesis of $(PPh_3)_2Pt(MesP{=}CPh_2)$ (**5**). According to its NMR spectra and its X-ray crystal structure determination, **5** presents an unusual Pt–P bonding situation.

Dark red crystals of **5** (mp 194–199 °C) were obtained in almost quantitative yield from the 1:1 reaction of $(PPh_3)_2Pt(C_2H_4)$ (**6**) with **1** in toluene at room temperature. Elemental analyses confirmed the proposed stoichiometry. A field desorption mass spectrum[10] indicated a monomeric structure. At room temperature, the ^{1}H and ^{31}P NMR spectra were broad; however, at −55 ± 1 °C, the ^{31}P NMR spectrum was sharp and showed interesting features (Table I). While the ^{31}P parameters of the two *nonequivalent* triphenylphosphine ligands are normal, those of ligand **1** are quite unusual: the δ value (−33.5) is shifted 266.5 ppm toward higher field from that of free **1**[1] (compare the relatively small shifts in η^1-bonded compounds[3,4] such as **2** (4.2 ppm

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(10) Field desorption mass spectrum: *m/z* 1034 $(C_{58}H_{51}P_3{}^{194}Pt)^{+\cdot}$; isotope pattern as expected for Pt; no fragmentation.

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