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REACTIVITIES OF METAL-CARBENES TOWARD ALKENES AND ALKYNES.(U)
NOV 80 T J KATZ, E B SAVAGE, S J LEE, M NAIR N00014-79-C-0683

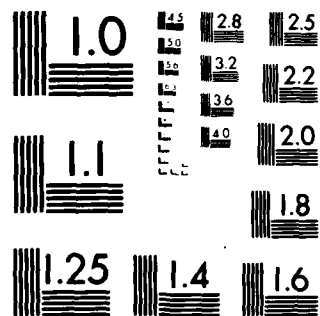
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Stabilized metal-carbenes like the P's in eqs 2 and 3 are very much more reactive toward phenylacetylene than toward cyclopentene (by a factor of 119-170) or cyclooctene (by a factor $> 10^4$). The result is strange but accords with 1 (also a stabilized metal-carbene) reacting much faster with acetylenes than with alkenes. In contrast, unstabilized metal-carbenes like the C's in eqs 4 and 5 are more reactive toward the cycloalkenes (cyclopentene 6-8 fold, cyclooctene ca. > 24 fold) than toward the acetylene. These figures were derived by analyzing the kinetics of eqs 1-5, (Contd)		

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Report Documentation Page 2, paragraph 20 continued (Abstract)

the simplest theory accounting for why phenylacetylene induces metatheses and why the yields and molecular weights of the polypentenamer formed by combining (phenylmethoxycarbene)pentacarbonyltungsten with phenylacetylene and cyclopentene decrease as the phenylacetylene concentration is increased. Evidence for the theory is found in gel permeation chromatograms of the polymers showing that polyalkenamer and polyacetylene units are linked.

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TECHNICAL REPORT NO. 2

Reactivities of Metal-Carbenes Toward Alkenes and Alkynes

by

Thomas J. Katz, Edward B. Savage, Steven J. Lee, Mridula Nair

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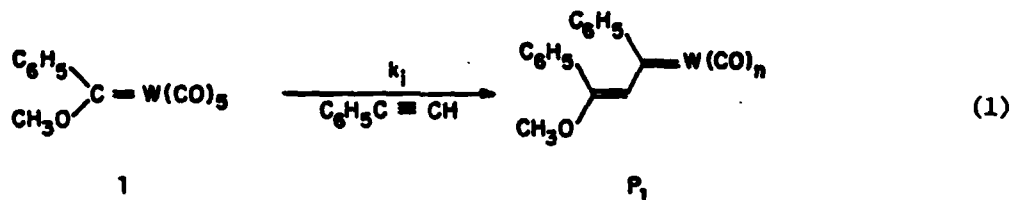
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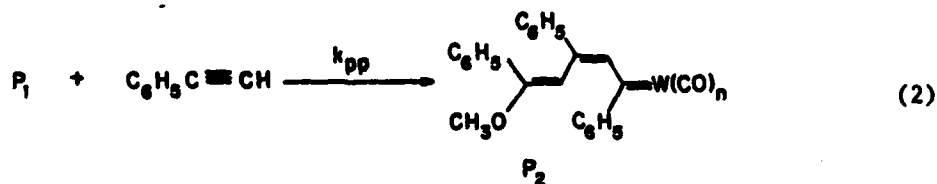
Sir:

In this paper we report data showing that stabilized metal-carbenes react much faster with acetylenes than with alkenes, while unstabilized metal-carbenes select oppositely. This data was obtained in accounting for acetylenes both inducing an otherwise ineffective metal-carbene to initiate olefin metathesis and also quenching the reaction.¹

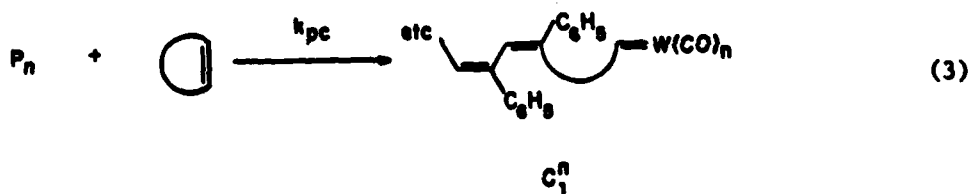
We suppose that a metal-carbene combines with an acetylene (like phenylacetylene) according to Scheme 1 of the preceding paper,¹ transforming the initial metal-carbene 1 into P₁ (eq 1 below). P₁ then reacts with



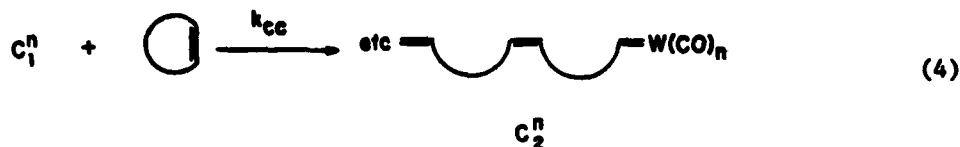
more of the acetylene according to eq 2; P₂ or a higher homologue, P_n,



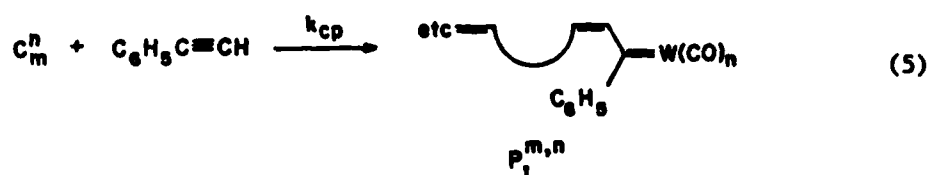
reacts with the olefin, say a cycloalkene, giving C₁ (eq 3); and C₁ then



propagates the metathesis in the usual way (eq 4). We suppose that



eq 5, a plausible analogue of the transformations above, whose action is



essentially the reverse of eq 3, accounts for the quenching.

Figure 1, depicting gel permeation chromatograms of polymers formed from cyclopentene and varying amounts of phenylacetylene, supports these ideas, for the intensity of absorption of 400 nm light (which measures polyphenylacetylene units² but not polyalkenamers³) parallels the intensity of refractive index changes (which measures the amount of bulk polymer, mainly polyalkenamer), implying that polyphenylacetylene and polyalkenamer units are attached.

An alternative theory for the quenching, involving either the acetylene or its polymer combining with I_2 , destroying its initiating ability, and thereby decreasing the number of polymer chains, might accommodate this observation, but it cannot be correct because as Figures 1 and 2 show, the molecular weights do not increase with phenylacetylene concentration as they should.⁵ However, if eq 5 applies and growing polyphenylacetylenes terminate easily (which seems plausible since polyacetylenes are commonly found to have much lower molecular weight^{6,7} than polyalkenamers^{4,9}), then capping a growing polyalkenamer with a phenylacetylene

will indeed increase the probability of its early termination.

The chromatograms also provide data for quantitative analyses of the equations. They are bimodal (presumably the high molecular weight material is largely polypentenamer⁹ and the low molecular weight material polyphenylacetylene⁶), and, as summarized in Table 1, the ratio of the areas under the high and low molecular weight peaks monitored by the light absorption is independent of the amount of phenylacetylene in the reaction mixture. This accords with our hypothesis since whether a polyphenylacetylene chain does or does not have a polyalkenamer attached to it depends on the concentration and reactivity of the cycloalkene, not the acetylene. The area ratio therefore measures this reactivity.

The fraction of the phenylacetylene polymerized (measured by the amount of light absorbed) and the total number of polymer chains (measured by the yields and molecular weights) are also both independent of the concentration of phenylacetylene, implying that the rate of initiation, eq 1, is independent of this concentration too.^{13,14}

Assuming that termination involves reaction of two P chains, the slope of the line in Figure 2 implies that $k_{cp}/k_{cc} = 0.125 \pm 0.03$ and the slope of the line in Figure 1 of the preceding paper that $k_{pp}/k_{pc} = 170 \pm 55$.^{15,16} (If termination were unimolecular in P, the corresponding figures would be 0.178 ± 0.04 and 119 ± 41 .)^{16,17}

Similar data for cyclooctene are less complete, but preliminary results imply that k_{cp}/k_{cc} is at least 4 times smaller and k_{pp}/k_{pc} at least 100 times larger.

Thus $\dot{C}'$'s, like other electrophiles,¹⁸⁻²⁰ react faster with alkenes than with the acetylene. But the stabilized metal-carbenes $\dot{P}$, unlike the unstabilized $\dot{C}'$'s, discriminate very much more and inversely, which is

Table 1. Summary of Yields and Polymer Distributions Resulting When Cyclopentene (100 eq), Phenylacetylene (x eq), and 1 (1 eq) are Combined at 50 °C for 21.5 h.

x	% yield polypentenamer ^a	$\bar{M}_w \times 10^{-3}$ ^b	$\bar{M}_n \times 10^{-3}$ ^b	% PPA at low mol. wt. ^c	% yield total PPA ^d
3.0	4.9	178	66	24.42±0.3	27
2.25	4.2	262	83	16.35±0.4	23
1.75	7.0	333	119	16.4 ±2	24
1.0	15.8	348	100	19.3 ±2	26
0.75	20.3	594	289	15.0 ±2	19
0.3	36.7	674	340	17.2 ±3	17

^aThe ratio of the weight of polymer (isolated by dissolving the product in CH₂Cl₂, precipitating with CH₃OH, and drying in a vacuum), diminished by the amount of polyphenylacetylene, and the weight of cyclopentene. ^bMeasured by gel permeation chromatography using toluene solutions and Waters Associates' μ -styrigel columns. The weights are one half those of polystyrenes that would exhibit the chromatograms observed (ref 11). The characteristics of the high-weight materials are listed. Those of the low-weight materials were measured as approximately " $\bar{M}_w$ " = (19.2±2) × 10³, " $\bar{M}_n$ " = (8.6±3) × 10³ (these are the weights of polystyrenes that would exhibit the chromatograms observed). Very low molecular-weight fractions may, however, have been excluded because (a) the instrument could not resolve very low molecular weights, (b) they may have been transparent, (c) they may have been lost during the isolation. ^cPPA = polyphenylacetylene. The ratio of the area under the low molecular weight peak in Figure 2 and the area under both peaks. For each sample the areas were measured on at least three chromatograms, and averages and standard deviations are listed. ^dBoth attached to and free of polyalkenamer. Measured by comparing the absorption at 400 nm with that of pure PPA. When x is small, small amounts of polyphenylacetylene of low molecular weight may be lost during the isolation.

strange,²¹ but accords with 1 (also a stabilized metal-carbene) reacting much more quickly with acetylenes than with alkenes.^{1,7,22,23}

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Thomas J. Katz. Edward B. Savage

Steven J. Lee. Mridula Nair

Department of Chemistry

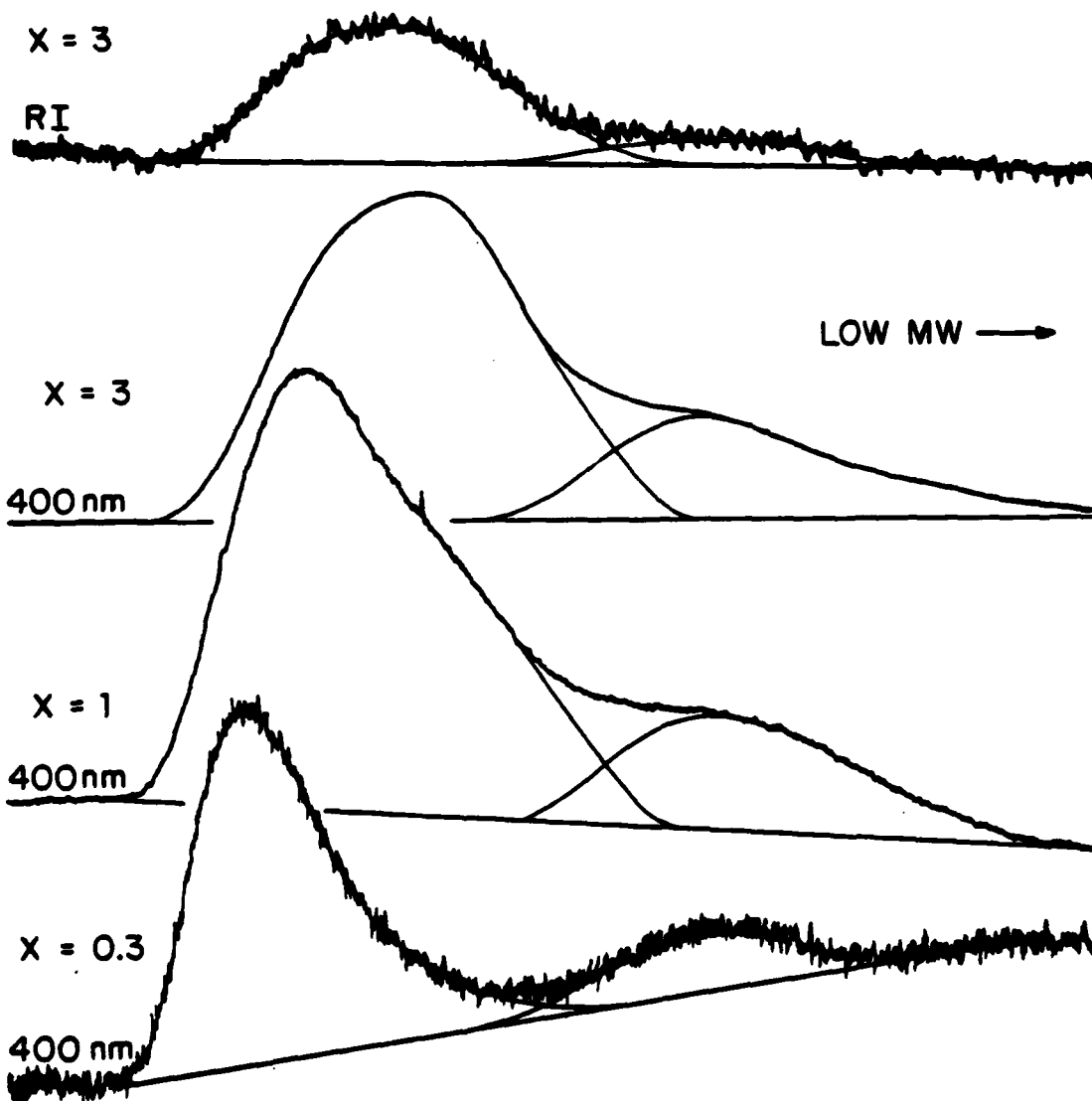
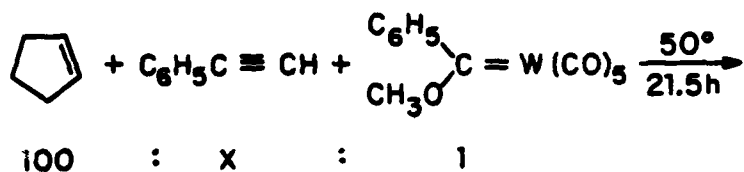
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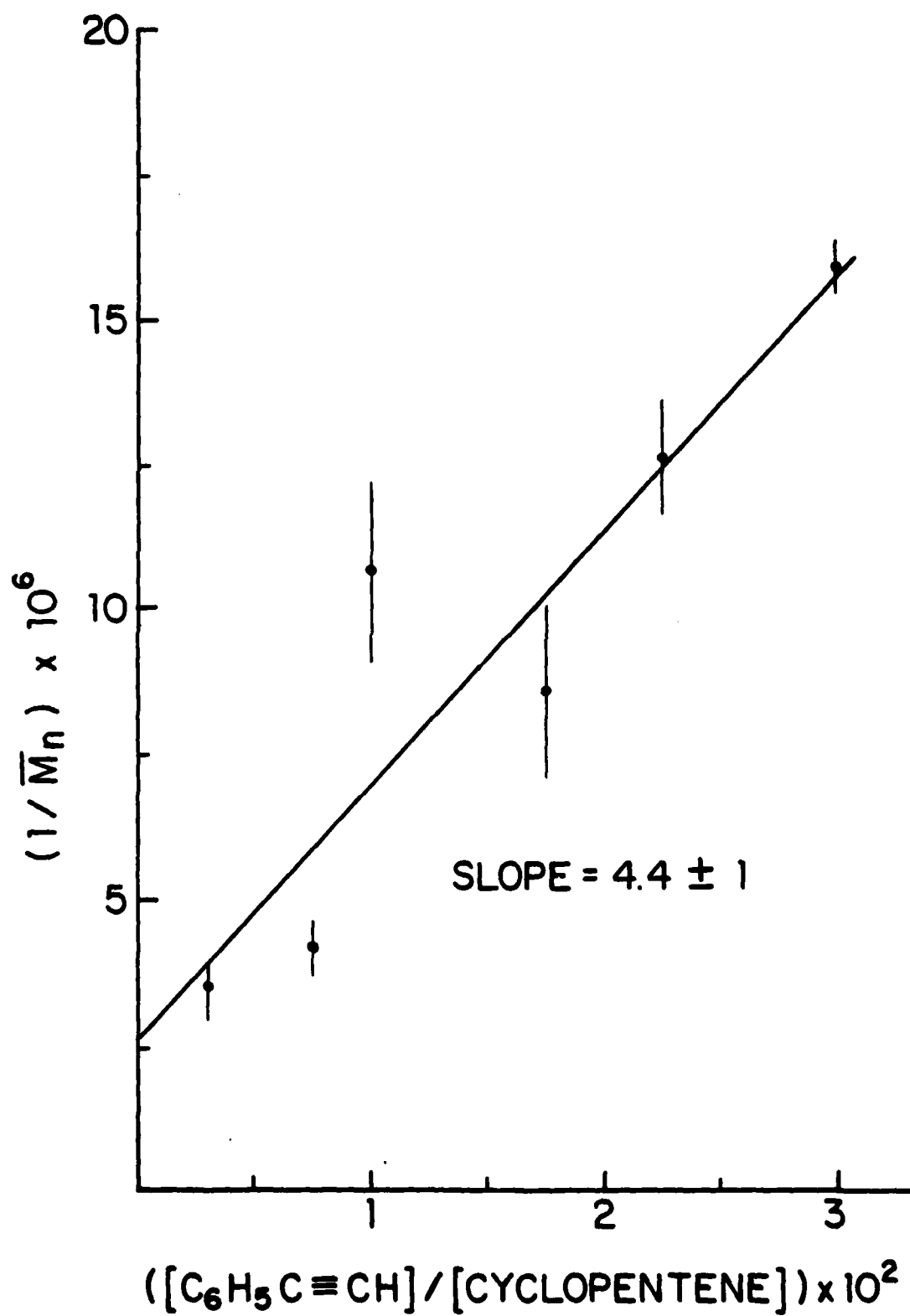
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Figure Captions

Figure 1. Gel permeation chromatograms in toluene on μ -styragel columns (exclusion limits 10^6 , 10^5 , 10^4 , 10^3 , 500 Å) of the polymer obtained from cyclopentene (100 equiv), phenylacetylene (x equiv), and $\frac{1}{2}$ (1 equiv) after 21.5 h at 50 °C. Analyses were by refractive index (top chromatogram) and by light absorption at 400 nm (bottom three chromatograms).

Figure 2. The relationship between the number average molecular weight of the polypentenamer and the ratio of phenylacetylene and cyclopentene combined with $\frac{1}{2}$ at 50°. The data are from Table 1.





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- (2) The electronic spectrum is published in Masuda, T.; Sasaki, N.; Higashimura, T. Macromolecules **1975**, 8, 717.
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- (5) They decrease also when phenylacetylene (10 mol) is added to (diphenylcarbene)pentacarbonyltungsten (1 mol) and cyclopentene (100 mol) from $\bar{M}_w = 5.3 \times 10^5$, $\bar{M}_n = 3.1 \times 10^5$ to $\bar{M}_w = 4.6 \times 10^4$, $\bar{M}_n = 1.7 \times 10^4$. The reactions were effected at 40 °C for 16 h, and the yields of polypentenamer were 46% and 22%.
- (6) $\bar{M}_n$'s for polyphenylacetylene made in a number of ways with metal catalysts range from about 1,000 to 15,000, and are commonly around 7,000.^{2,7,8}
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- (14) The number of polymer chains is 30% of the lowest number of moles of $\frac{1}{2}$ used in the experiments in Table 1 and 3% of the highest number.
- (15)
$$\frac{1}{\bar{x}_n} = \frac{k_{cp}}{k_{cc}} \frac{[C_6H_5C\equiv CH]}{[cyclopentene]} \left[\frac{R^{1/2}(1-R)}{2-(R+R^{1/2})} \right],$$
 where $\bar{x} = \bar{M}_n/68$, and R = the ratio of the area under the low molecular weight peak in Figure 1 divided by the area under both peaks.

$$(16) \quad \frac{1}{y} = \frac{k_{pp}k_{cp}}{k_{pc}k_{cc}} \left(\frac{1}{y'} - 1 \right) \frac{[C_6H_5C\equiv CH]_0}{[cyclopentene]_0} + 1, \text{ where } y \text{ and } y' \text{ are the}$$

fractional yields of polyalkenamer and polyphenylacetylene respectively.

Subscript zero refers to initial concentrations.

$$(17) \quad \frac{1}{\bar{x}_n} = \frac{k_{cp}}{k_{cc}} \frac{[C_6H_5C\equiv CH]R}{[cyclopentene]}$$

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(23) P'_2 's are presumably less stabilized than $\frac{1}{2}$, which is why they initiate metatheses that $\frac{1}{2}$ does not.

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