

mation were not unique to *cis*-2-butene was demonstrated through the use of *cis*-3-hexene in place of *cis*-2-butene. After 30 min, 0.03% of ethyl *trans*-2-ethylcyclopropanecarboxylate¹¹ was obtained.

In summary, we have demonstrated that metal-carbene intermediates can be generated from noncarbenoid precursors under metathesis conditions. These metal-carbene intermediates can be selectively trapped by Michael acceptors such as ethyl acrylate. Interestingly, ethyl acrylate does not quench the metal complex promoted conversion of **1** into **2**. This provides added support to the concept that the complex generated from phenyltungsten trichloride and aluminum trichloride can react with olefins by more than one mechanistic path.

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Retrocarbene Additions. Dissection of Alkyl-Substituted Cyclopropanes under Metathesis Conditions¹

Sir:

While the addition of carbenes and carbenoid-type intermediates to double bonds has been an extensively studied and much discussed subject,² relatively little is known about the reverse process. Formal retrocarbene additions have been observed in a few isolated cases, where the cyclopropane was part of a highly strained fused ring system.^{3,4} We now wish to report that the well-established olefin metathesis catalyst⁵ derived from phenyltungsten trichloride and aluminum chloride⁶ will promote retrocarbene additions from certain simple cyclopropanes under mild conditions.

Two pieces of knowledge formed the basis for this investigation. First, alkyl-substituted cyclopropanes were not nor-

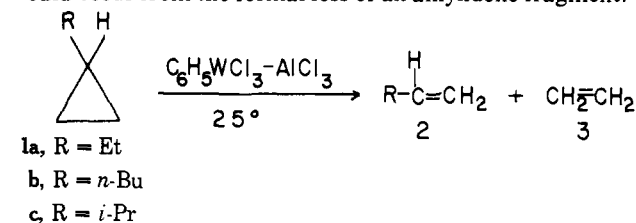
Table I. Yields of Olefins Obtained in the Retrocarbene Addition Reactions of Simple Monosubstituted Cyclopropanes

Cyclopropane	% conversion ^a	Yield of olefins ^b		Ratio of CH ₂ =CH ₂ , RCH=CH ₂ / CH ₂ =CH ₂
		RCH=CH ₂ , %	CH ₂ =CH ₂ , %	
1a	83	1-butene, 73 ^c	11	6.8
1b	80	1-hexene, 60	9	6.7
1c	72	3-methyl-1-butene, 66	10	6.6

^a The percent conversion was determined by measuring the amount of unreacted cyclopropane. ^b The olefin yields were based on the amount of cyclopropane unrecovered. ^c In addition, 2% of 3-hexene was found.

mally observed as products of olefin metathesis, even though metal-carbene complexes were commonly invoked as chain-carrying intermediates.^{5b,7} Secondly, certain platinum derivatives were known to add to cyclopropanes to form metalcyclobutanes.⁸ This prompted us to speculate that simple alkyl-substituted cyclopropanes might react with certain metathesis catalysts to form metalcyclobutanes which, under the reaction conditions, would dissociate into metal-carbene complexes⁹ and olefins as per the proposed^{5b,7} mechanism for olefin metathesis. In order to test this hypothesis, we allowed the soluble complex formed from phenyltungsten trichloride and aluminum trichloride (1:1) to react with cyclopropane in chlorobenzene at -78 °C. An immediate and vigorous evolution of ethylene occurred. Significantly, no trace of propylene could be detected.

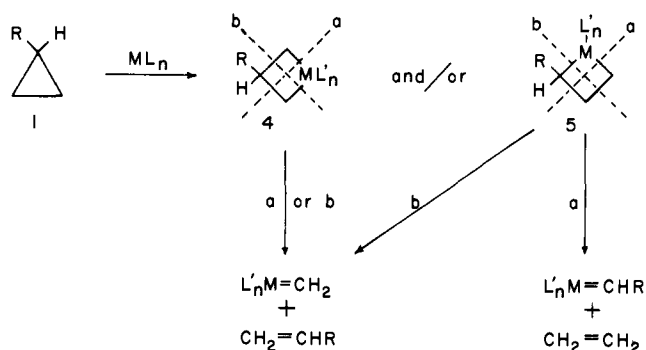
As part of a preliminary study of the generality of such "retrocarbene additions", we carried out a quantitative study of the catalyzed fragmentation of a series of simple cyclopropanes (**1a-c**). All three of the compounds studied gave a mixture of the appropriate 1-alkene (**2**), which would result from the formal loss of methylene, and ethylene (**3**), which would occur from the formal loss of an alkylidene fragment.¹⁰



These reactions were carried out in sealed Carius tubes at room temperature in dimethyl ether-chlorobenzene (5:1 v/v) as solvent with a 200:1 molar ratio of the cyclopropane to the tungsten catalyst. The reactions were allowed to run for 2.5 h. Table I summarizes the results of this study. As can be noted from Table I, after 2.5 h ca. 70-80% of the cyclopropane had been catalytically fragmented. The total yields¹¹ of retrocarbene addition products ranged from 76-86%. Again, no cyclopropane to olefin *isomerization* products were detected.

The ratio of 1-substituted olefin to ethylene indicated a high degree of selectivity in the fragmentation process. Mechanistically, two processes could be envisaged, which would account for the observation. One possibility would involve the direct extraction of a carbenoid unit by the metal complex to yield an olefin and the metal-carbenoid complex directly. Such a process, while possible, has little in the way of precedent. A more attractive mechanistic picture would involve initial insertion into a carbon-carbon bond of the monosubstituted cyclopropane to yield a metalcyclobutane by some "oxidative addition" type process.^{12,13} Ample precedent exists for such an insertion reaction in the studies of McQuillan and Powell, who reported⁸ that platinum inserted primarily into the least-substituted bond of monosubstituted cyclopropanes to

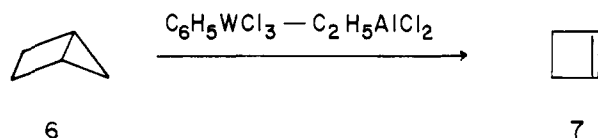
yield platinum-containing, four-membered rings. An analogous process with **1** would produce **4** ($M = \text{tungsten}$) and/or **5**. On the basis of analogy to the platinum studies, **4** would be ex-



pected to be the major product. Breakdown of **4**, as proposed for olefin metathesis, could only produce the metal-bonded carbene and a monosubstituted olefin, since cleavage paths a and b are degenerate. The fragmentation of **5** would produce the same products from path b as the fragmentation of **4**. In contrast, cleavage of **5** via path a would yield ethylene. The fact that ethylene was observed¹⁰ as a product suggests at least partial formation of **5**, if a metallocyclobutane is involved as a critical intermediate. In terms of this speculative mechanistic picture, it is not possible to say whether the high specificity for formation of a monosubstituted olefin is due to the preferential generation of **5** followed by selective cleavage of **5**, with path b predominating, or whether it is due to preferential formation of **4**.

Relative to the fate of the metal-carbene fragment, which would result from either mechanism, less is known.¹⁰ In the catalyzed retrocarbene addition from ethylcyclopropane, 2% of *trans*-3-hexene was observed. In principle, this could result from either carbenoid dimerization or the metathesis of the 1-butene formed in the metathesis.^{7,14} In practice, we demonstrated that 1-butene did not yield *trans*-3-hexene when exposed to the same tungsten catalyst for the same period of time in the same solvent system.

In a more practical vein, we have found that bicyclo[2.1.0]pentane (**6**),¹⁵ when treated with the complex formed from phenyltungsten trichloride-ethylaluminum dichloride (1:1), gave a 70% yield of cyclobutene (**7**). This indicates that



metal-complex-promoted retrocarbene additions may prove to be synthetically useful in the preparation of certain unusual olefins.

In summary, we have demonstrated that certain alkyl-substituted cyclopropanes are readily fragmented by phenyltungsten trichloride-aluminum chloride complexes. Since this complex is a well-established metathesis catalyst, the implication is that simple, alkyl-substituted cyclopropanes would not survive some of the conditions used to promote olefin metathesis. Various synthetic and mechanistic applications of our discovery are currently under study.

Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation.

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Cyclopropane-Olefin Cross Metathesis

Sir:

A relatively clean retrocarbene addition of carbenoids from simple, alkyl-substituted cyclopropanes has recently been discovered in our laboratories.¹ We have also recently reported² that electron-deficient, α,β -unsaturated esters can efficiently trap certain metal-complexed carbenes generated in olefin metathesis reactions. Conceptually combining the logic behind these two relatively independent discoveries led to the hypothesis that a divalent carbon fragment should be able to be transferred from an alkyl-substituted cyclopropane (**1**) to an electron-deficient, conjugated olefin (**2**) to yield an alkene (**3**) and an electron-deficient cyclopropane (**4**). We now wish to

