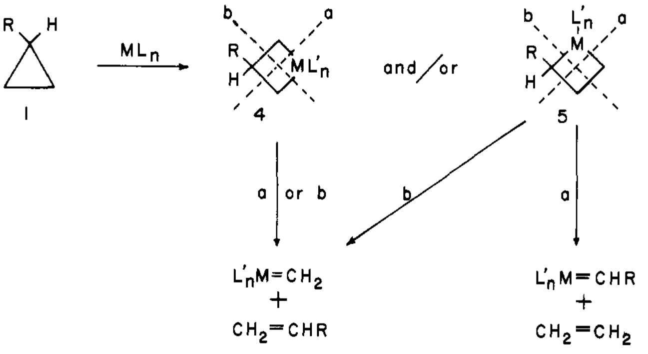
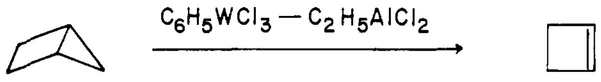
yield platinum-containing, four-membered rings. An analogous process with **1** would produce **4** (M = tungsten) and/or **5**. On the basis of analogy to the platinum studies, **4** would be expected to be the major product. Breakdown of **4**, as proposed for olefin metathesis, could only produce 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 observed[10] 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.



6 7

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.

References and Notes

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(9) For evidence of the intermediacy of such metal-carbene complexes, see P. G. Gassman and T. H. Johnson, ref. 1.
(10) An alternate, but seemingly less likely explanation, would involve formation of ethylene via dimerization of two one-carbon carbenoid intermediates. However, the formation of small amounts of *trans*-3-hexene (vide post) is consistent with the formal loss of an alkylidene fragment from the alkyl-substituted cyclopropane to form ethylene directly. The low yield of ethylene resulted in a question concerning material balance. The remainder of the "methylene" fragment appears to be incorporated into a higher molecular weight, intractable material.
(11) Yields were determined vs. an internal standard (*n*-hexane) by GLC analysis on an 11 ft × ⅛ in. silver nitrate-ethylene glycol on 60/80 Chromosorb P column at room temperature. All products were isolated and identified via spectroscopic comparison with authentic samples.
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Paul G. Gassman,* Thomas H. Johnson
Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

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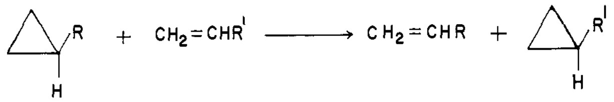
Cyclopropane-Olefin Cross Metathesis

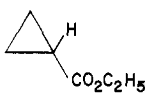
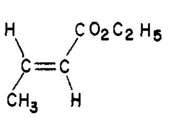
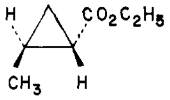
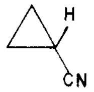
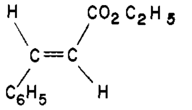
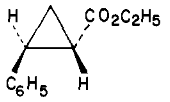
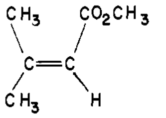
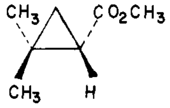
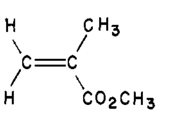
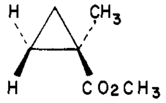
Sir:

A relatively clean retrocarbene addition of carbenoids from simple, alkyl-substituted cyclopropanes has recently been discovered in our laboratories.[1] We have also recently reported[2] 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



1 2 3 4

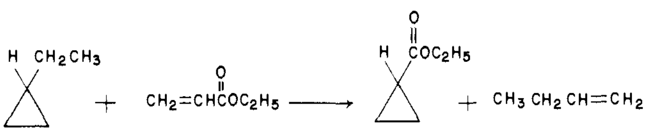
Table I. Yields of Cyclopropanes Obtained in the Ethylcyclopropane–Olefin Cross Methathesis, Utilizing Both Homogeneous and Heterogeneous Catalysis

Olefin	Cyclopropane	% yield[a,b]	% yield[b,c]
$CH_2{=}CHCO_2C_2H_5$	 7	14	12
	 8	12	10
$CH_2{=}CHCN$	 9	9	7
	 10	2	<1
	 11	11	8
	 12	13	10

[a] Catalysts derived from phenyltungsten trichloride and ethylaluminum dichloride under homogeneous conditions in chlorobenzene. [b] Yields determined by VPC *vs.* an internal standard. [c] Catalyst derived from phenyltungsten trichloride and ethylaluminum dichloride and used under heterogeneous conditions in hexane.

report that such cyclopropane-olefin cross metathesis reactions can be accomplished in the presence of the catalysts formed from the reaction of phenyltungsten trichloride with either aluminum trichloride or ethylaluminum dichloride.

In a preliminary study, a mixture of ethylcyclopropane (**5**) and ethyl acrylate (**6**) was treated with the soluble complex[3] formed from phenyltungsten trichloride and aluminum trichloride (1:1). Workup of the reaction mixture gave 4% of ethyl cyclopropanecarboxylate (**7**) in addition to an undetermined amount of 1-butene (**8**).[4] The formation of **7**, while


5 6 7 8

formally establishing the principle of cyclopropane-olefin cross metathesis, left much to be desired in terms of yield. In an attempt to improve this process, we explored the use of other catalyst systems. In this regard, a new complex derived from phenyltungsten trichloride and ethylaluminum dichloride[5] was found to be a significant improvement.

In a typical experiment, 2 ml of a solution of the catalyst (<0.0001 mol) in chlorobenzene[6] was added to 0.01 mol of ethylcyclopropane and 0.01 mol of a suitable α,β-unsaturated ester or nitrile (Michael acceptor) in 30 ml of deoxygenated chlorobenzene. The reactions were then stirred for ca. 12 h, diluted with ethanol, filtered, and analyzed by VPC, utilizing cyclododecane as an internal standard. Table I lists the yields of cyclopropanes obtained by this method. Firm structural assignments were made in all cases through isolation of the products and comparison of their spectral properties with those of authentic samples. In the case of the esters, hydrolysis to the corresponding acids was first accomplished with base in order to facilitate isolation.

As can be seen from Table I, the yields obtained in this cyclopropane-olefin cross metathesis, while low when viewed as a useful synthetic method, are quite substantial when considered in terms of a sequential methylene abstraction-methylene addition. Clearly, the isolation of **7**–**12**[7] firmly establishes the existence of the cross-metathesis process. Furthermore, the formation of these cyclopropanes offers substantial support to the hypothesized generation of a metal-carbene complex in the retrocarbene addition from alkyl-substituted cyclopropanes[1] and to the mechanistic picture proposed for the quenching of olefin metathesis by Michael acceptors.[2]

As an additional aspect of this investigation, we treated a hexane slurry of phenyltungsten trichloride with a hexane solution of ethylaluminum dichloride. The black precipitate which formed was collected by filtration and washed thoroughly with hexane in the absence of oxygen. This precipitate was utilized as a catalyst in hexane (slurry) to promote the cyclopropane-olefin cross metathesis. The yields for the heterogeneous process are also listed in Table I. As can be noted from the table, the yields with the heterogeneous catalyst system are only slightly lower than those obtained with the homogeneous catalyst system. As far as these results relate to retrocarbene additions from olefins, the quenching of olefin metathesis, and cyclopropane-olefin cross metathesis, the implication is that similar types of intermediates are generated in both homogeneous and heterogeneous catalytic processes. We believe that in all three of the above named reactions a highly nucleophilic metal-carbene intermediate is formed.

We are continuing to explore the scope and mechanistic ramifications of this cyclopropane-olefin cross metathesis reaction. In particular, work is in progress which is designed to increase the yields to the point where this reaction will be synthetically useful.

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

References and Notes

(1) Paper 50 on The Chemistry of Bent Bonds. For the previous paper in this series, see P. G. Gassman and T. H. Johnson, *J. Am. Chem. Soc.*, preceding paper in this issue.

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(4) As established in ref 1, the reaction of **5** with the phenyltungsten trichloride-aluminum trichloride complex produced 1-butene in 73% yield.

(5) Ethylaluminum dichloride was purchased from Alfa Products as a 25% solution in hexane and used without further purification.

(6) The catalyst system was prepared by the addition of a solution of 0.5 ml of 25% ethylaluminum dichloride (in hexane) to 0.37 g of phenyltungsten trichloride in 20 ml of deoxygenated chlorobenzene. After 5 min, the clear yellow supernatant liquid was removed from the remaining solid. Aliquots of this homogeneous solution were used in the ratio of 2 ml per 0.01 mol of the appropriate cyclopropane. This constituted at least a 100:1 ratio of cyclopropane to catalyst.

(7) In the cross metathesis reaction between ethylcyclopropane and ethyl acrylate, no ethyl 2-ethylcyclopropanecarboxylate was observed. While no special efforts were made to determine the presence or absence of this possible by-product, we feel that 2% would have been readily observed, had it been present in the reaction mixture.

Paul G. Gassman,* Thomas H. Johnson
Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

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