Hrung and Dr. B. Gorewit for many helpful discussions. We wish to acknowledge support of this research project by the Office of Naval Research, the Robert A. Welch Foundation (Grant No. A-328), and the Texas Agricultural Experiment Station (H-1668).

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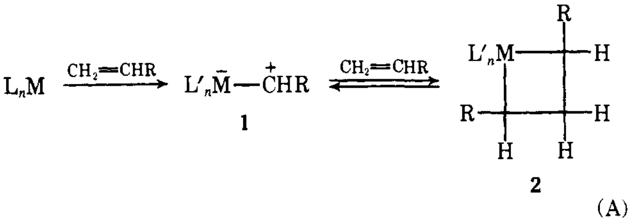
Received June 24, 1976

The Relationship of Polarization in Metal–Carbene Complexes to the Degenerate Metathesis of Terminal Olefins[1]

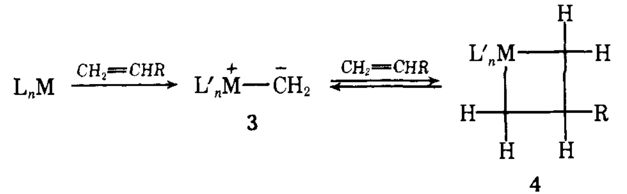
Sir:

Differing explanations have appeared for the degeneracy observed in the metathesis[2] of terminal olefins. We now wish to report experimental evidence which supports the contention that, at least in the case of certain tungsten-based catalysts, the degenerate metathesis of terminal olefins is due to the polarization of the chain-carrying metal–carbene complex. In addition, we suggest that this polarization results in nucleophilic character on carbon and significant positive charge distribution to the metal.

The degenerate nature of the metathesis of terminal olefins has been well established by the excellent use of isotopic labeling experiments.[3] Not only have these olefins been shown to metathesize in a degenerate manner, but it has been demonstrated that they metathesize so rapidly that the presence of terminal olefins may effectively inhibit the metathesis of internal olefins.[4] The degeneracy of terminal olefin metathesis has been discussed in terms of steric interactions.[4,5] Alternatively, it has been implied that this degeneracy is the result of a highly selective addition of a polarized intermediate to a terminal olefin.[5,6] The latter rationalization has been viewed in terms of process A,[5,6] which occurs with intermediate formation of **2** via addition of **1** to a terminal olefin.[7] At least as attractive is process B, which involves the addition of **3** to a terminal olefin to produce the intermediate **4**.[8] Distinguishing between process A and process B amounts to distinguishing between electrophilic and nucleophilic addition to a terminal olefin.[9] It also amounts to determining whether the transition metal complex reacts with the terminal olefin to form **1** or **3** in the generation of the initial metal–carbene complex.

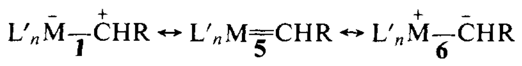


(A)



(B)

If a simple method were available which would permit experimental determination of the polar character of **5**, that is, whether **6** or **1** was the major resonance contributor, the problem could be readily solved.[10] In principle, this could be accomplished through a cross-metathesis reaction between 2-butene and a terminal olefin. In practice, the metathesis of the terminal olefins was so rapid that effective cross-metathesis with internal olefins was not readily observed.[4,11] Thus, an alternate method was needed for the generation of significant amounts of **5** in the presence of a terminal olefin. If this could be accomplished, examination of the products of the reaction would allow a distinction to be made between the various mechanistic possibilities. Formation of **7**, which would not be expected to metathesize in the presence of a terminal olefin, would require **8** as a precursor. The formation of **8** would be inconsistent with either a sterically controlled mechanism or with process A. Furthermore, it would only be consistent with **6** being the major resonance contributor. If only **9** were observed, **10** would be implicated as the crucial intermediate and either process A or a sterically controlled mechanism would be required.



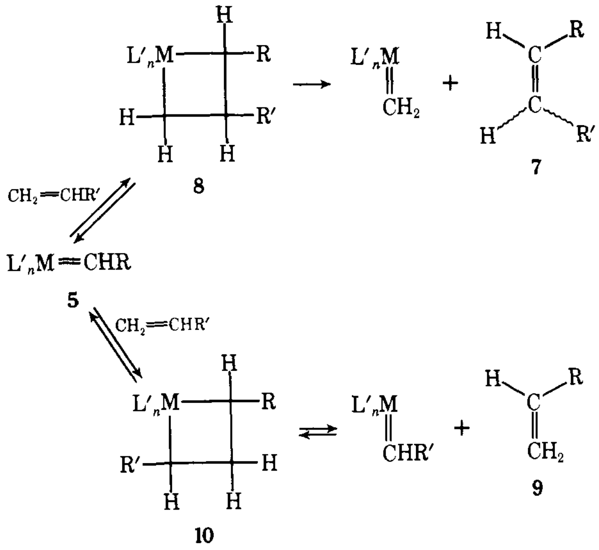
$$\underset{1}{L'_n\overset{-}{M}-\overset{+}{C}HR} \leftrightarrow \underset{5}{L'_nM{=}CHR} \leftrightarrow \underset{6}{L'_n\overset{+}{M}-\overset{-}{C}HR}$$

Fortunately, our recent discovery of phenyltungsten trichloride–aluminum trichloride promoted retro-carbene additions[12] offered an attractive possibility for the generation of

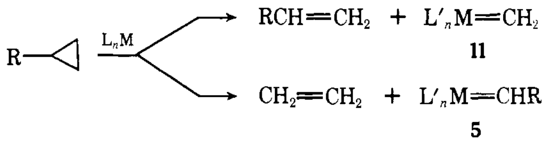
Table I. Product Yields Obtained in the Cross Metathesis Reaction of C-Alkyl Substituted Metal-Carbene Complexes with Terminal Olefins

Terminal olefin	3-Olefin formed	% yield[a]	% yield[b]	Trans/cis
1-Butene	3-Hexene	35	c	3.4
1-Pentene	3-Heptene	30[d,e]	71	3.5
1-Hexene	3-Octene	29[d,e]	74	3.5

[a] Yield based on 1-olefin. All yields are determined by GLC analysis vs. cyclododecane as an internal standard. [b] Yield base on unrecovered 1-olefin. [c] Since 1-butene was generated from the ethylcyclopropane, this value was meaningless. [d] In addition, 4% of 3-hexene was formed. [e] Trace amounts of 4-octene and 5-decene were also observed in the experiments which utilized 3-heptene and 3-octene, respectively.



significant concentrations of C-alkyl substituted tungsten-carbene complexes. From our previous work,[12] we knew that ethylcyclopropane (R = C_2H_5) gave 1-butene (73%) and ethylene (11%). We suggested that **11** and **5** were formed as the other fragmentation products in a 6.6:1 ratio. If this hypothesis were correct, we would have in hand a viable method of generating significant concentrations of **5**.



$$\text{R}\!-\!\triangleleft \xrightarrow{L_nM} \begin{cases} \text{RCH}{=}\text{CH}_2 + \text{L}'_n\text{M}{=}\text{CH}_2 \ (\mathbf{11}) \\ \text{CH}_2{=}\text{CH}_2 + \text{L}'_n\text{M}{=}\text{CHR} \ (\mathbf{5}) \end{cases}$$

In a typical experiment, 3.5 equiv of ethylcyclopropane and 1 equiv of a terminal olefin in chlorobenzene were treated with 0.005 equiv of the complex generated from phenyltungsten trichloride-aluminum trichloride (1:1) at −20 °C with vigorous stirring in an inert atmosphere. After 30 min, the reaction was quenched by the addition of ethanol. Isolation of the products and identification by GLC, IR, and NMR analyses established that olefins of general type **7** were formed in significant amounts.[13] The results obtained when 1-butene, 1-pentene, and 1-hexene were used as the terminal olefins are shown in Table I. As shown by the data in Table I, the metal-carbene complex, **5**, which was formed in the metalysis of ethylcyclopropane was efficiently captured by the 1-olefin present in solution.[14] If the amount of **5** equaled the amount of ethylene observed, the yields of 3-olefins based on capture of **5** would be 91, 78, and 75% for addition to 1-butene, 1-pentene, and 1-hexene, respectively.[15]

The formation of good yields of 3-olefins in these reactions requires not only the intermediacy of **5** (R = C_2H_5), but also of the highly selective addition of **5** to the 1-olefin to produce **8**. This is inconsistent with terminal olefin degeneracy being determined by either process A or by a sterically controlled mechanism.[16] This study provides additional evidence that the metal-carbene complexes involved in olefin metathesis reactions promoted by phenyltungsten trichloride-aluminum trichloride have resonance structures of general formula **6** as major contributors.[17]

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

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(7) Distinguishing between process A and a mechanism governed by steric interactions would be difficult, since both explanations would predict the formation of **2** as part of the chain process.

(8) The question of whether there is an initial step, in which the metal-carbene intermediate complexes with the olefin, is not discussed as part of this study. While our results do not require such a complexation step, neither do they rule out such a possibility.

(9) This is not meant to imply that we envisage a purely stepwise addition of the intermediate metal-carbene complex to the terminal olefin. Such polarized additions could involve significant formation of both new bonds in the transition state for the reaction.

(10) In part, this question has been answered by the trapping of intermediates generated in the metathesis of *cis*-2-butene and *cis*-3-hexene by Michael acceptors. P. G. Gassman and T. H. Johnson *J. Am. Chem. Soc.*, **98**, 6055 (1976).

(11) This observation, by itself, points to **6** as the major resonance contributor *if polarization of the intermediate metal-carbene complex is the major factor* in determining the degeneracy of terminal olefin metathesis. If **1** was the major resonance contributor, arguments based purely on patterns of electrophilic additions to olefins would suggest that **1** should add at least as well to an internal olefin, such as *cis*-2-butene, as to a terminal olefin. Unfortunately, steric factors are not easily evaluated relative to this point.

(12) P. G. Gassman and T. H. Johnson, *J. Am. Chem. Soc.*, **98**, 6057 (1976).

(13) In a control experiment, it was demonstrated that the complex derived from phenyltungsten trichloride-aluminum trichloride (1:1) did not produce any metathesis of *cis*-2-pentene in the presence of 1-hexene over a 30-min period.

(14) It is presumed that **11** also reacted with the 1-olefin. However, such an addition would only lead to a degenerate process.

(15) These represent maximum yields based on the premise that all of the ethylene formed was detected. If it was assumed that the yield of ethylene was actually 27% (100% − % of 1-butene), the respective yields would be 37, 32, and 31%. These represent minimum yields.

(16) We caution that, at this time, we have only established this principle for certain tungsten based metal-carbene complexes.

(17) For a well-established example of such polarization in a stable metal-carbene complex see R. R. Schrock, *J. Am. Chem. Soc.*, **97**, 6577 (1975).

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Solid Phase Cosolvents[1]

Sir:

We have recently introduced a technique termed, "triphase catalysis", in which a solid phase catalyst is used to accelerate certain aqueous-organic phase reactions.[2] This method was based on the use of appropriately substituted polystyrene-ion-exchange resins capable of ionic bonding to the water soluble component of the reaction.[3] It occurred to us that if similar triphase catalytic processes could be carried out employing uncharged and neutral polymers, this would constitute a much more general technique worthy of extensive exploitation. Specifically, we reasoned that resins which acted as cosolvents might function as catalysts for aqueous-organic phase reactions by providing (1) a common phase with a high effective concentration of potential reactants and/or (2) an internal resin phase having a microenvironment significantly different from that of the external liquid phases. In this same regard, it also seemed likely that solid phase cosolvents might be useful in accelerating certain types of reactions taking place in a single phase (organic or aqueous phase). Based on these ideas, we have initiated a program aimed at developing insoluble polymers which exhibit *cosolvent-like* properties.

We now wish to report our preliminary results with the preparation of graft copolymer **1** and its use as a solid phase cosolvent in (1) the hydrolysis of 1-bromoadamantane and *tert*-butyl chloride and (2) the displacement by phenoxide ion on 1-bromobutane.