Table I. Observed Ionization Energies IE_n of $H_2C{=}S$, Their Assignment by Different Calculations ($-\epsilon_J^{SCF}$, ab Initio SCF; GF, Greens' Function Approximation; RHF, Restricted Hartree Fock Open Shell Method; CI, Configuration Interaction), and the Total Energies for the Neutral Ground State

State	IE_n[a]	$-\epsilon_J^{SCF}$		GF	RHF	CI
$\tilde{X}$ $^2B_2$	9.38	$3b_2$(n)	9.44	9.12	8.25	9.08[b]
$\tilde{A}$ $^2B_1$	11.76	$2b_1(\pi)$	11.25	11.63	10.31	11.49[b]
$\tilde{B}$ $^2A_1$	13.85	$7a_1(\sigma)$	14.62	13.82	13.46	13.75[b]
$\tilde{C}$ $^2B_2$	15.20	$2b_2$	17.40	15.80	15.81	15.78[c]
$\tilde{D}$ $^2A_1$	19.9	$6a_1$	21.97	19.45	21.12	20.22[c]
$\tilde{E}$ $^2A_1$		$5a_1$	28.87		27.42	26.00[c]
$\tilde{S}$ 1s hole			2502.3		2471.3	
2s hole			243.6		233.6	
2p hole			180.5		169.7	
C 1s hole			307.9		296.0	
E_{total} (eV)[d] RHF	11 878.067 97					
CI[c]	11 885.336 84 (upper bound)					
CI[b]	11 886.276 37					

[a] Maximum of band or most intense subband. [b] CEPA. [c] PNO-CI. [d] 1 au = 27.21167 eV.

Table II. Changes in RHF Gross Atomic Populations upon Ionizations $H_2C{=}S \rightarrow H_2C{=}S^{\cdot +}$

Atom	$\tilde{X}(^2B_1)$	$\tilde{A}(^2B_1)$	$\tilde{B}(^2A_1)$	$\tilde{C}(^2B_2)$	$\tilde{D}(^2A_1)$	$\tilde{E}(^2A_1)$
H	−0.126	−0.116	−0.136	−0.217	−0.171	−0.142
C	−0.114	−0.225	−0.237	−0.070	−0.133	−0.156
S	−0.635	−0.542	−0.489	−0.497	−0.525	−0.561

approach (CEPA),[8] and many-body Greens' function[9] (GF) methods for the ground state geometry.[3a] The three lowest ionization energies of $H_2C{=}S$ are already well reproduced by the ab initio SCF orbital eigenvalues: a comparison with the RHF and CI values demonstrates that correlation and rearrangement energy contributions are of opposite sign and nearly cancel each other (Table I). Obviously, about 75% of the correlation contribution to the ionization energies in these states are accounted for by the CEPA calculations, and—considering the imposed limitations[10] in the size of the basis set and in the configuration expansion—deviations of only 0.1 to 0.3 eV from the experimental values are rather satisfactory. On the contrary, anomalous behavior of correlation energy contributions is found for the higher excited states of H_2CS^+ because some doubly excited (shake-up) configurations become nearly degenerate with the singly-ionized parent configurations.[8]

The RHF open-shell calculations also demonstrate (Table II) that simple orbital pictures[6] no longer adequately represent the electron distribution in the individual radical cation states. Although the $\tilde{X}(^2B_2)$ state expectedly shows the highest sulfur contribution and the $\tilde{C}(^2B_2)$ state exhibits a nearly constant carbon population, altogether a rather delocalized cation charge is calculated for all valence ionizations.

In conclusion, it might be noted that thioformaldehyde has been established in 1971 as a constituent of the interstellar medium.[11]

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(9) Cf. ref 7; the results for $H_2C{=}S$ are a private communication by W. v. Niessen, L. S. Cederbaum, W. Domcke, and H. Diercksen.

(10) The Gaussian type orbital basis sets are of the size: 9s, 5p, 2d for C, 11s, 7p, 2d for S, 5s, 1p for H. All valence electrons have been correlated and threshold of 2×10^{-4} hartree has been used for selecting configurations. Atomic calculations with these parameters suggest that also for the ground state of $H_2C{=}S$ about 75% of the valence correlation energy has been covered (Table I). For another CI treatment of $H_2C{=}S$ cf. P. J. Bruna, S. D. Peyerimhoff, R. J. Buenker, and P. Rosmus, *Chem. Phys.*, **3**, 35 (1974).

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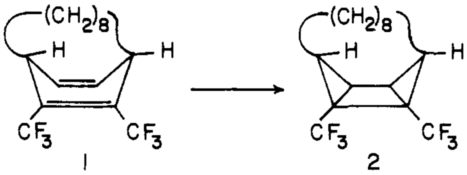
Quenching of Olefin Metathesis. Evidence for the Generation of Metal–Carbene Intermediates from Noncarbenoid Precursors[1a]

Sir:

Recently, we reported[1b] the conversion of the nonconjugated diene system **1** into the cyclobutane derivative **2** through interaction with the well-established metathesis catalyst[2] derived from phenyltungsten trichloride and aluminum chloride. This same catalyst system was found to be very effective in the

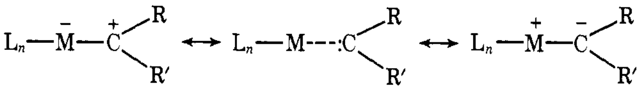


1 2

conversion of certain other cyclobutyl derivatives into nonconjugated diene systems.[1] Rather than clarifying the mechanistic picture of olefin metathesis, these results served as a complicating factor, which tended to detract from the currently accepted theory that many olefin metathesis reactions proceed through a metallocyclobutane.[3] This metallocyclobutane was hypothesized to arise through the addition of a chain-carrying metal–carbene species to an olefin.[3,4] While substantial supportive evidence exists for this type of cycloaddition mechanism, relatively little is known about the origin and nature of this crucial chain-carrying, metal–carbene intermediate. In those cases where the added metathesis catalyst was a metal–carbene complex, the origin of the chain-carrying intermediate seemed obvious. However, when the added catalyst was not a metal–carbene complex, neither the mechanism of formation nor even the presence of a metal–carbene intermediate has been established. We now wish to report experimental evidence which shows that some olefin metatheses do involve the formation of metal–carbene complexes from noncarbenoid precursors. This premise is based on the trapping of such carbenes by Michael acceptors. Indeed, we have shown that compounds such as ethyl acrylate are so efficient at reacting with certain metal–carbene species that they can completely quench olefin metathesis.

Typically, the intermediacy of a carbene is established through the isolation of a cyclopropane derived from the addition of the carbene to a suitable olefin. The presence of metal–carbene complexes has also been established via such trapping experiments.[3b,5] Casey and co-workers have shown that certain metal–carbene complexes, which can be used as metathesis catalysts, do give cyclopropanes with a wide variety of olefins.[3b] In one recent instance, the isolation of a cyclopropane, which was not formed directly from a preformed metal–carbene complex, was reported.[3e] However, in this case the trapped carbene moiety was formed through an exchange reaction with a preformed metal–carbene complex during metathesis.[6]

In considering metal–carbene complexes, we can envisage three resonance forms as shown below. The active carbon center can be envisaged as being either nucleophilic (**5**) or electrophilic (**3**). For those metal–carbene complexes where R and/or R′ invoke the direct bonding of the reactive center to a heteroatom, electrophilic character is generally observed.[5,8] Interestingly, those metal–carbene complexes generated in metathesis reactions might be expected to show very different properties, since they would be metal–alkylidene complexes. In support of this concept, it has been demonstrated that an isolated metal–alkylidene complex exhibited nucleophilic character.[9] These observations would suggest that any metal–carbene complex formed as an intermediate in a metathesis reaction might be expected to possess a nucleophilic carbon and, therefore, might be readily trapped by a Michael acceptor.

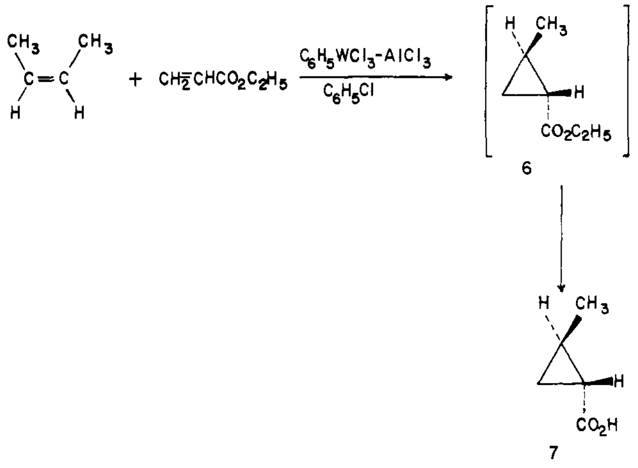


3 **4** **5**

In order to test this theory, we utilized the complex derived from phenyltungsten trichloride–aluminum trichloride (1:1), which is a known metathesis catalyst.[2] First, we established that this homogeneous complex[1,2] would readily metathesize *cis*-2-butene to a mixture of *cis*- and *trans*-2-butene, and 2-pentene to a mixture of 2-butene, 2-pentene, and 3-hexene in our hands. When we attempted to carry out these same metathesis reactions in the presence of ethyl acrylate, no metathesis of either *cis*-2-butene or 2-pentene was observed. *The presence of ethyl acrylate had completely quenched the metathesis process.* Other compounds which were found to efficiently quench olefin metathesis under the conditions described above were diethyl fumarate, ethyl cinnamate, and ethyl crotonate. All of these quenchers are Michael acceptors. The necessity of having an electron-deficient double bond present for quenching was supported by the observation that neither acetone, ethyl acetate, diethyl ether, nor dimethoxyethane would inhibit metathesis.

We were now forced to question whether the Michael acceptors were destroying the initial complex formed from the phenyltungsten trichloride and aluminum trichloride or capturing a metal–carbene complex formed from the reaction of the homogeneous catalyst with the olefin. In principle, the latter possibility could be readily established by the isolation of products containing the cyclopropyl moiety. However, since the metathesis of simple olefins is thought to invoke a metal–carbene complex in a chain reaction, the concentration of such a complex in a metathesis reaction is probably extremely small. Thus, the isolation of cyclopropane derivatives was expected to present major difficulties.

In an attempt to isolate a cyclopropane derivative, 1 mol of *cis*-2-butene, 1 mol of ethyl acrylate, and 0.01 mol of the soluble complex formed from phenyltungsten trichloride–aluminum trichloride (1:1) in chlorobenzene was sealed in a Carius tube and the homogeneous reaction mixture was allowed to stand at room temperature for 30 min. Since a trace component was sought, the reaction mixture was poured into dilute hydrochloric acid and the esters present in solution were hydrolyzed to the corresponding acids. The acidic material was isolated by extraction with sodium bicarbonate solution, neutralization, and re-extraction with diethyl ether. Evaporation of the ether gave an acidic residue, which on preparative VPC gave 40 mg (ca. 0.04%) of *trans*-2-methylcyclopropanecarboxylic acid (**7**). The spectral properties of this material were identical in all respects with those of an authentic sample.[10] The isolation of **7** required the formation of **6** in the reaction mixture. This would necessitate the addition of ethylidene to the ethyl acrylate. Clearly, the *cis*-2-butene must have reacted with the complex derived from the phenyltungsten trichloride–aluminum trichloride to give a tungsten–ethylidene complex. It should be noted that while **6** was formed, no metathesis of the *cis*-2-butene could be detected. This means that the reaction of the tungsten–ethylidene complex with the Michael acceptor was far more rapid than the reaction of this complex with the *cis*-2-butene. Similar results were obtained when the metathesis of *cis*-2-butene was run for 15 min and ethyl acrylate was then added. It was observed that the metathesis of the *cis*-2-butene was immediately quenched, and ethyl *trans*-2-methylcyclopropanecarboxylate[11] was again formed. That this quenching reaction and cyclopropane for-



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-ethylcyclopropanecarboxylate[11] 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,

Acknowledgment. We are indebted to the National Science Foundation for Grant MPS75-01984, which supported this investigation.

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Retrocarbene Additions. Dissection of Alkyl-Substituted Cyclopropanes under Metathesis Conditions[1]

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 catalyst[5] derived from phenyltungsten trichloride and aluminum chloride[6] will promote retrocarbene additions from certain simple cyclopropanes under mild conditions.

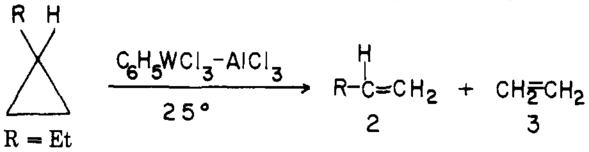
Two pieces of knowledge formed the basis for this investigation. First, alkyl-substituted cyclopropanes were not normally observed as products of olefin metathesis, even though metal–carbene complexes were commonly invoked as chain-carrying intermediates.[5b,7] Secondly, certain platinum derivatives were known to add to cyclopropanes to form metallocyclobutanes.[8] This prompted us to speculate that simple alkyl-substituted cyclopropanes might react with certain metathesis catalysts to form metallocyclobutanes which, under the reaction conditions, would dissociate into metal–carbene complexes[9] 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.

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

Cyclopropane	% conversion[a]	Yield of olefins[b]		Ratio of
		$RCH{=}CH_2$, %	$CH_2{=}CH_2$, %	$RCH{=}CH_2/CH_2{=}CH_2$
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.

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]



1a, R = Et
b, R = *n*-Bu
c, R = *i*-Pr

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 yields[11] 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 metallocyclobutane by some "oxidative addition" type process.[12,13] Ample precedent exists for such an insertion reaction in the studies of McQuillan and Powell, who reported[8] that platinum inserted primarily into the least-substituted bond of monosubstituted cyclopropanes to