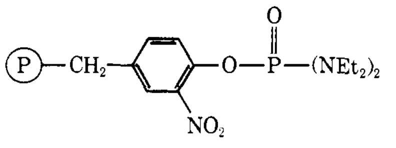

VIII

phosphorimidic amide) is indicated. Application of this method to the parent monomeric metaphosphate ion is in progress.

Acknowledgments. We thank Professor G. Kenyon for advice and Professor F. H. Westheimer for informing us of his own results prior to publication. Financial support was provided by the Fulbright Commission's Program of Cultural Cooperation between the U.S.A. and Spain and the Research Corporation.

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(14) This compound was characterized by the expected spectroscopic features and gave satisfactory elemental analyses.
(15) It is possible that the actual phosphorylating agent is complexed with dioxane; at present we are unable to distinguish between such a complex and solvated metaphosphate.
(16) Visiting Fulbright Scholar on leave from the University of Valencia, Valencia, Spain.

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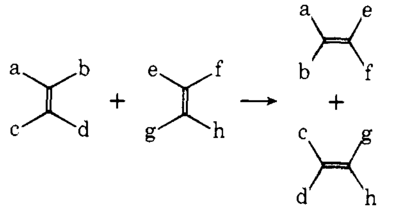
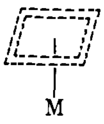
The Mechanism of the Olefin Metathesis Reaction

Sir:

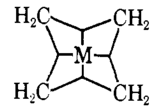
The olefin metathesis reaction generalized as in eq 1 is effected by catalysts usually containing tungsten, molybdenum, or rhenium.[1] On the basis of the gross structural change, mechanism I was suggested,[2,3] but to account for the three facts, (1) that no cyclobutane has been found to evolve from the reaction, (2) that no cyclobutane has been found to enter into the reaction,[4a,5] and (3) that cyclobutane has no accessible valencies for bonding to metals, seemed to require either unusual theories for the bonding in I[6] or the proposition that the key intermediate be instead the multicentered species II.[4a,7] An alternative mechanism postulates the transformation shown in eq 2,[8] but this would also be unusual.



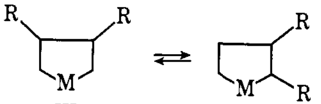
(1)



I



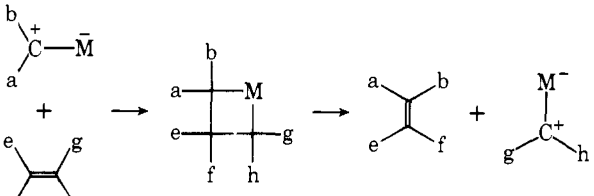
II



III

(2)

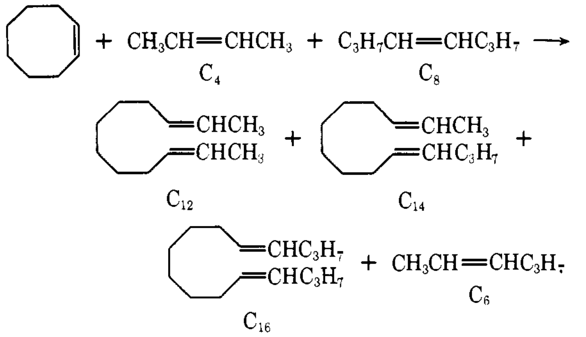
Probably none of these schemes is correct and the actual mechanism is the chain reaction 3. Since metal-carbenes[9] and four-membered rings containing metals[10] are known species and additions to olefins are common, this proposal requires no unusual theoretical explanation, and we show below that it accounts for all the known facts about olefin metathesis. The importance of this theory is that it can be applied widely to make predictions. The major difficulty is finding a way to prove it.[11]



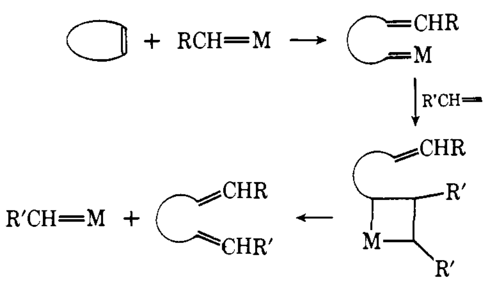
IV

(3)

Consider the following experimental test, the reaction of a cyclic olefin like cyclooctene with a mixture of 2-butene and 4-octene. According to any of the schemes the C_{12}, C_{14}, and C_{16} dienes (eq 4) should form ultimately, but according to the schemes in which I, II, and III form in the rate-determining step, the ratio of C_{14} and C_{12} or of C_{14} and C_{16} would have to be zero initially. In contrast, Scheme I indi-



Scheme I



cates that if R and R′ serve only as labels, the mechanism of eq 3 would initially make the major product the one that conventionally would not form at all. Anomalous cross products[17] were previously recognized in only one case,[19] by Hérisson and Chauvin, who found them after short reaction between cyclopentene and 2-pentene.[16]

Cyclooctene (4.13 mmol), *trans*-2-butene (1.4 mmol), and *trans*-4-octene (3.03 mmol) were added at 0° to a catalyst solution prepared by incubating[21] $Mo[(C_6H_5)_3P]_2Cl_2(NO)_2$ (0.058 mmol) in chlorobenzene (2.1 ml) with methylaluminum sesquichloride (0.33 mmol) for 1.5 hr at room temperature. The solution was warmed to 25°, and samples were periodically quenched with water and analyzed by GLPC.[22] After 11 min, the molar ratio of C_{14} and C_{12} (symbolized C_{14}/C_{12}) (eq 4) was 1.34 and C_{14}/C_{16} 3.0, while C_6/C_4 was only 0.027 and C_6/C_8 0.014. The amount of cyclooctene consumed was 5 ± 3%.[23] With time the product ratios changed toward equilibrium.[21] Extrapolated to zero time, C_{14}/C_{12} was 1.30 ± 0.08 and C_{14}/C_{16} was 3.32 ± 0.3. Since these are not zero, mechanisms like those involving I, II, and III in which union of two olefin molecules is rate-determining are excluded.

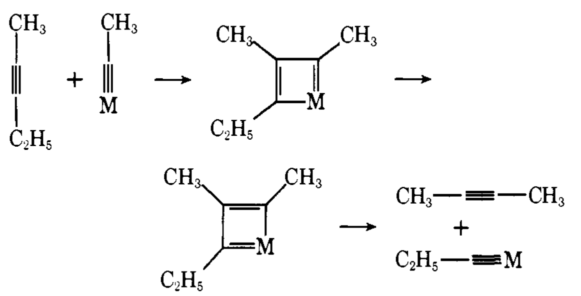
However, if the displacement reaction, eq 5, were rate-

$$(RCH{=}CHR)_2M + R'CH{=}CHR' \longrightarrow (RCH{=}CHR)(R'CH{=}CHR')M \qquad (5)$$

determining, the data above (and the kinetics[21,24]) could be accounted for by the conventional mechanisms, and, as proposed previously by Calderon,[25] this hypothesis would account for the high molecular weights of the polymers formed early in the reactions of cycloolefins.[26] It is easier, however, to see how the ratios of products in metatheses of cycloolefins and unsymmetrically substituted acyclic olefins are explained by the carbene mechanism.

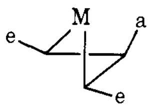
Consider the reaction of cyclooctene with 2-hexene. A catalyst solution (2.5 ml) prepared as above from $Mo[(C_6H_5)_3P]_2Cl_2(NO)_2$ (0.019 mmol) and methylaluminum sesquichloride (0.11 mmol) was combined with cyclooctene (1.9 mmol) and 2-hexene (1.9 mmol) at 0°. Samples were quenched with water and analyzed by GLPC for the ratios C_{16}/C_{14}, C_{12}/C_{14}, and C_8/C_6.[27] A graph of C_{16}/C_{14} against C_8/C_6 showed that when C_8/C_6 was zero, C_{16}/C_{14} was 0.29 ± 0.02 and C_{12}/C_{14} was 0.27 ± 0.02. Again, since these figures are not zero, mechanisms involving rate-determining bimolecular union of two olefins are excluded. But consider the deviation of the ratios of C_{12}, C_{14}, and C_{16} product from 1:2:1. As seen here and in the metatheses of cyclooctene[16] and cyclopentene[26d] with 1-pentene as well as in related cases,[20,26c] the conventional product always forms to an extent greater than 50% and in increasing amount up to 95%[26d] the more the ends R and R′ in RCH=CHR′ differ. According to schemes in which eq 5 is rate determining, this is because different olefins are displaced from the metal at different rates. According to the mechanism of eq 3, the selectivity is a consequence of the factors that stabilize one carbonium ion more than another.[28] A corollary is the prediction that cycloalkenes unsymmetrically substituted on the double bond will yield alternating rather than random polymers.

The mechanism of eq 3 accounts most acceptably for the metathesis of acetylenes, like 2-pentyne.[29] The conventional interpretation seems impossible to reconcile with the stability of cyclobutadiene-cobalt complexes.[30] Equation 6 interprets the reaction as proceeding through the intermediacy of metal carbynes.[31]

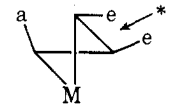


(6)

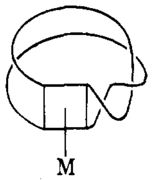
We indicate below how other facts can be interpreted according to the mechanism of eq 3. The stereochemical course can be interpreted by presuming that steric interactions are minimized if the carbene substituent enters the four-membered ring[32] (1) equatorially and (2) not adjacent to an equatorial substituent. That is, if the metal-carbene enters vertically, V should be favored over VI because of the starred interaction,[33] accounting for the observation that



V



VI



VII

cis-2-butene and 3-hexene are formed faster than the trans isomers from *cis*-2-pentene[2,34] and that *cis*-2-butene possibly forms faster than trans from propylene.[35]

The formation of large rings and catenanes from smaller cyclic olefins[36] can be interpreted as proceeding not through twisted intermediates like VII[36c,d] but by cyclization of the terminal carbene upon an internal double bond of a long chain.[37] The same path accounts for the products containing $(C_4H_6)_n$ fragments in the oligomers of cycloocta-1,5-diene or cyclododeca-1,4,7-triene[15,39] or in their adducts with 1-pentene.[16]

The high molecular weight[26] of the polymers formed early in the reaction of cycloolefins is a natural consequence of Scheme I.[15,16]

The formation of cyclopropane and methylcyclopropane from ethylene[40] can also be accounted for with eq 3 and known analogies.[14,41]

The mechanism suggests that initiators for olefin metathesis be sought by synthesizing simple alkyl-substituted metal-carbene species[15,42] and four-membered rings.[43]

Acknowledgments. We are grateful to the National Science Foundation (NSF-GP30669X) for its support and to E. A. Ofstead and N. Calderon for enlightenments.

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(22) The C_{12}, C_{14}, and C_{16} products were identified by their ^1H NMR and mass spectra. *n*-Heptane was the GLPC internal standard.

(23) There are two reasons for believing that the cross products do not form by the acyclic olefins cleaving polyoctenemer, $[-CH{=}CH(CH_2)_6-]_n$, the polymer of cyclooctene. One, since cyclooctene is largely unconsumed, the polymer would have to be more reactive than cyclooctene toward acyclic olefins, which is unlikely. Two, the selectivity, for example the absence of cross products in the reactions of terminal olefins with cycloolefins, could not be accounted for.

(24) A mechanism accounting for the data above is eq i, but it fails to account for the kinetics being first order in metal.[21]

$$RCH{=}M + R'CH{=}M \rightleftarrows RCH{=}CHR' + 2M \qquad (i)$$

(25) Reference 1b, p 131.

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(33) Key: e = equatorial, a = axial.

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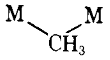
Alkylation and Structural Rearrangement of the Bridging Carbonyl Ligand in $HFe_3(CO)_{11}^-$. The Synthesis of $HFe_3(CO)_{10}(COCH_3)$

Sir:

The interaction of strong carbocation reagents with polynuclear carbonyl anions conceivably might lead to a number of interesting structural features such as metal-alkyl-metal bridges, **1**, and O-alkylation of basic carbonyl groups, **2**. Since neither of these are known in metal carbonyl chemistry, we have recently initiated studies on the alkylation of polynuclear carbonyl species. In this report we present some novel findings on the chemistry of trinuclear iron species.



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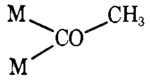

2

The salt $[DMTED][Fe_3(CO)_{11}]$ (DMTED = *N,N'*-dimethyltriethylenediamine +2 cation) was prepared by a simple adaptation of Hieber and Brendel's preparation of $[Ni(phen)_3][Fe_3(CO)_{11}]$.[1] Treatment of the DMTED salt with slightly more than an equimolar quantity of CH_3SO_3F in acetonitrile followed by addition of diethyl ether and filtration yields a solution of crude product, from which solvent is removed under vacuum. The solid is washed with benzene and recrystallized from toluene–acetonitrile. A 0.20-g sample of the resulting $[DMTED][Fe_3(CO)_{11}(CH_3)]_2$ was dissolved in 50 ml of CH_3CN, HCl gas was passed over the solution, solvent was removed under vacuum, and the dark red-purple product was sublimed at 45° under a hard vacuum. Anal. Calcd for $HFe_3(CO)_{11}CH_3{\cdot}H_2O$: C, 28.28; H, 1.19; O, 37.67; Fe, 32.87. Found: C, 28.09; H, 1.21; O, 37.21; Fe, 32.67. (Water may have been introduced at the analytical laboratory, as we find no evidence for its presence in any of our experiments.) In a sealed capillary decomposition begins around 135°. A cryoscopic molecular weight determination in benzene solution, conducted under strictly air-free conditions,[2] gave a value of 520. The highest mass peak of appreciable intensity occurs at 492 mass units, in agreement with the parent ion of $HFe_3(CO)_{11}CH_3$. For a large number of peaks, such as those at 492, 464, 436, 408, 380, and 352, a feature is observed two mass units lower with an intensity 0.2 of its high-mass partner. This intensity ratio agrees with the presence of ^{54}Fe at 6% abundance in a Fe_3 cluster. The existence of this cluster over a wide mass range indicates a closed iron triangle rather than an open chain structure.[3] Definitive evidence for the presence of a metal hydride linkage is provided by the presence of a high field resonance 18.2 ppm from TMS. The methyl group is observed at −4.23 ppm with intensity 2.7 of the hydride signal.

A crystal 0.30 × 0.32 × 0.35 mm sealed in a fused quartz capillary was submitted for X-ray structure determination.[4] (See paragraph at end of paper regarding supplementary material.) As may be seen in Figure 1, the molecule con-