formed into each product. Yield and conversion data were determined by GLC on 20% Silicone GE XE-60 on 60/80 Chromosorb P and 20% 1,2,3-tris(2-cyanoethoxy)propane on 60/80 Chromosorb W columns. Standard mixtures of reactants and products were analyzed in order to determine the relationships between signal responses and molar ratios. The organic products were isolated by preparative GLC and were identified by their infrared, ^{1}H NMR, and mass spectra.

(4) D. Evans, J. A. Osborn, and G. Wilkinson, *Inorg. Synth.*, 11, 99 (1968).

(5) In a typical experiment conducted at room temperature, 7 ml of a deoxygenated solution of 4-pentenal, 0.11 ml (1.12 mmol), in chloroform was added via hypodermic syringe to a flask containing 0.29 g (0.11 mmol) of $Rh^{I}(acac)(C_2H_4)_2$[6] under argon. The closed flask was then stirred under an argon atmosphere. The resulting yellow solution turned brown with time. The mixture was monitored periodically by GLC. In experiments conducted in ethylene-saturated chloroform, the aldehyde-chloroform solution was saturated with ethylene at 1 atm prior to its addition to the flask containing the rhodium compound. Experiments employing **1** were conducted in a similar manner. Dichloromethane was also found to be a suitable solvent for these reactions. Control experiments demonstrated that the 0.75% ethanol inhibitor in the "Baker Analyzed Reagent" chloroform employed in these experiments did not adversely affect product yields or conversions. Comparable yields and conversions were achieved in experiments employing either *freshly purified* ethanol-free $CHCl_3$ or fresh reagent $CHCl_3$ containing 0.75% ethanol. Utilization of chloroform samples that had decomposed slightly on standing led to the formation of double bond migration products when 4-pentenal was treated with **1**. Compound **6** could not be separated from 4-pentenal on the TCEP or Silicone GE XE-60 GLC columns. Therefore, mixtures of the two compounds were collected and their molar ratios in the mixtures were determined by ^{1}H NMR analysis when experiments employing **2** and 4-pentenal were conducted.

(6) R. Cramer, *J. Am. Chem. Soc.*, **86**, 217 (1964).

(7) See R. Cramer, *Acc. Chem. Res.*, 1, 186 (1968), for a review of the role of rhodium catalysts in alkene isomerizations.

(8) An unusually brief account of the addition of acetaldehyde to 1-heptene in an unspecified low yield, catalyzed by **1**, has been reported. No reaction conditions or methods of product characterization were included.[9]

(9) I. S. Kolomnikov, M. B. Erman, V. P. Kukolev, and M. E. Vol'pin, *Kinet. Katal.*, **13**, 252 (1972).

(10) C. Walling, "Free Radicals in Solution", Wiley, New York, N.Y., 1957, p 273 ff.

(11) L. K. Montgomery and J. W. Matt, *J. Am. Chem. Soc.*, **89**, 6556 (1967).

(12) Precedent for the formation of a 4-pentenoylmetal complex was first observed in organocobalt chemistry: R. F. Heck, *J. Am. Chem. Soc.*, **85**, 651 (1963).

(13) Reductive elimination via carbon-carbon coupling has recently been proposed to occur in reactions of acyl chlorides with alkylrhodium complexes to generate ketones: (a) J. Schwartz and J. B. Cannon, *J. Am. Chem. Soc.*, **96**, 4721 (1974); (b) L. S. Hegedus, P. M. Kendall, S. M. Lo, and J. R. Sheats, *ibid.*, **97**, 5448 (1975).

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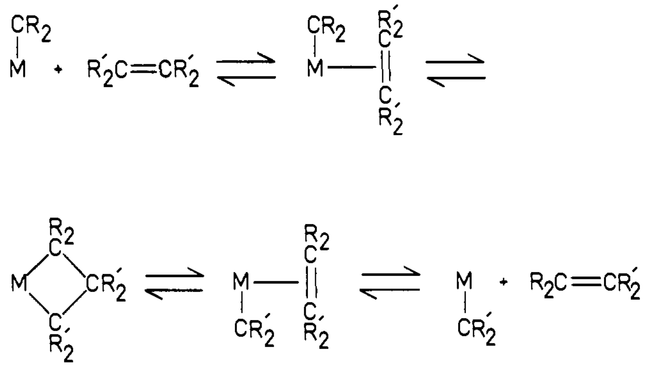
Olefin Metathesis Reaction. III.[1] Mechanistic Considerations

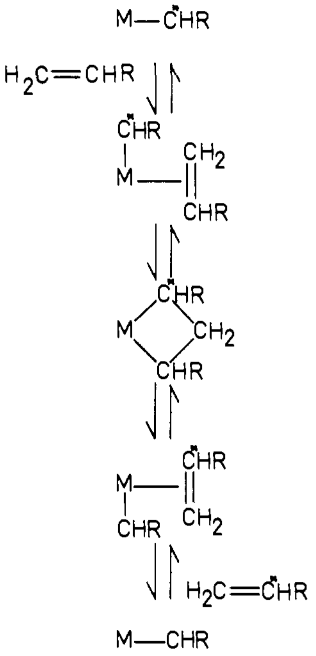
Sir:

After a period in which a plethora of reaction mechanisms were advanced for the remarkable catalytic olefin metathesis reaction,[2] there now appears to be a growing consensus that metal carbene and metallocyclobutane intermediates are involved in the reaction, at least for tungsten-based catalysts, as shown in Scheme I. The model tungsten carbene studies by Casey and Burkhardt,[3] the alkylidene exchange studies by Katz and McGinnis[4] and by Grubbs et al.,[5] and our[1] observations on the basic tungsten chemistry have strengthened the chain carbene concept originally advanced by Herisson and Chauvin.[6] Additionally, the recent *isolation* of a simple M-CH_2 carbene[7] demonstrates the plausibility of metal carbene intermediates that do not bear electronegative substituents on the carbene carbon atom. We report here some methylene transfer reactions that are consistent with this basic mechanistic concept, provide additional insight to the variability in the basic reaction with slight modifications in catalyst, and establish a stereochemical feature of these catalysts that must be fully explained in any mechanism proposed for olefin metathesis.

Scheme I



Scheme II



Metathesis catalysts based on WCl_6 reportedly do not metathesize terminal olefins.[2] From purely mechanistic considerations, we proposed[1] that terminal olefins do in fact metathesize in all catalytic systems but in a relatively selective and nonproductive (or degenerate) fashion so as to reform the original terminal olefin as in Scheme II. We have established that the catalyst derived from WCl_6 + C_2H_5OH + $4C_2H_5AlCl_2$ interacts more strongly with a terminal than with an internal olefin. The metathesis rate of *cis*-2-pentene with this catalyst system is sharply reduced on addition of 1-nonene (See Figure 1). This result is in full accord with the general finding that the association constants for olefin-metal complexes are larger for terminal than for internal olefins.[8] To determine if there would in fact be an interchange of terminal CH_2 and CD_2 groups in view of the incisive demonstration (Figure 1) of strong interaction of the terminal olefin with the catalyst, we decided to test our basic proposal[1] by following the fate of a terminal olefin mixture of 1-hexene and 1-heptene-*1,1*-d_2 (or 1-pentene-d_{10}) in the presence of catalysts prepared from the various WCl_6-R_xM recipes.[2]

The heterogeneous catalyst[9] derived from WCl_6 + 2*n*-C_4H_9Li[10] effected exchange of terminal CH_2 and CD_2 groups with 1-hexene and 1-heptene-*1,1*-d_2; 1-hexene-*1,1*-d_2 and 1-heptene were the only hydrocarbons other than the starting olefins and traces of productive metathesis products (vide infra) detected by GC mass spectral analysis. There was no evidence of H-D exchange via a carbon-hydrogen bond scission. An analogous CH_2-CD_2 exchange was ob-

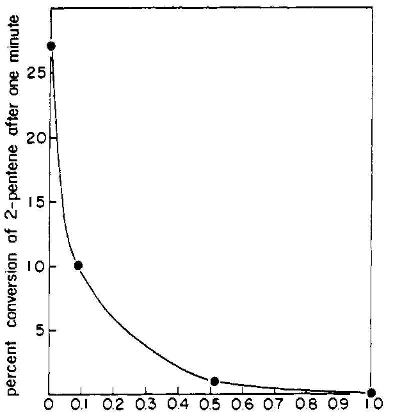


Figure 1. The precent conversion of 2-pentene after 1 min vs. moles of 1-nonene/moles of total olefin. At equilibrium, the conversion of 2-pentene is 50%.

served with the $WCl_6 + 2C_2H_5AlCl_2$ catalyst recipe[11,12] using the 1-pentene-d_{10} and 1-hexene mixture. The ethanol modified catalyst $WCl_6 + C_2H_5OH + 4C_2H_5AlCl_2$,[13] which in our hands[9] is the most active of the various WCl_6 based catalysts, was found to be complicated by a terminal olefin isomerization reaction; however, we have learned from Dr. N. Calderon[14] that he has successfully established the exchange of terminal CH_2 and CD_2 groups for a 1-pentene-d_{10} and 1-pentene mixture.

These reults confirm the postulated[1] reaction mode of terminal olefins in these WCl_6-based catalyst recipes. This qualitative feature of these metathesis systems is not just explicable in terms of the carbene chain mechanism but is expected in this mechanism (as well as in alternative mechanisms). For a terminal olefin $RCH{=}CH_2$, the carbene chain mechanism would allow for either ethylene and $RCH{=}CHR$ formation or terminal CH_2 group interchange between olefins. Not fully predicted or explained in intimate mechanistic[1] detail (vide infra) is the dominance of nonproductive over productive metathesis in these catalyst systems. We find the ratio of nonproductive to productive metathesis to be about a thousand to one at near equilibrium for CH_2-CD_2 exchange in the aluminum and lithium based catalyst systems. This "product ratio" was lowered to ca. one hundred to one when the catalyst derived from $WCl_6 + Zn(CH_3)_2$[9] was treated with 1-pentene-d_{10} and 1-hexene. Olefin reaction products here were 4-octene-d_{16}, 4-nonene-*1,1,1,2,2,3,3,4*-d_8,[15] 5-decene, 1-pentene-*2,3,3,4,4,5,5,5*-d_8, and 1-hexene-*1,1*-d_2.

The difference in the ratios of nonproductive to productive metathesis with the catalysts examined for this specific stereochemical facet of the metathesis reaction may be mechanistically significant.[16] A possible explanation for the difference is a variability in the catalysts' stereochemistry which might be derived from the nature of the interaction[1] of the non-transition metal halide ($AlCl_3$, LiCl, and $ZnCl_2$) with the tungsten complex. However, we wish to emphasize a point, largely ignored in discussions of metathesis catalysts and metathesis reaction mechanism, that illustrates the difficulty in comparing data for different catalyst recipes even though based on a single transition metal compound like WCl_6 or a "unified" couple such as WCl_6-$C_2H_5AlCl_2$ in which relative reagent ratios may vary. A single compositional and stereochemical metathesis catalyst may not necessarily be generated even from a set catalyst recipe.[17] Catalytic reactions which are often competitive with metathesis and which range from olefin isomerization to olefin dimerization to arene (solvent) alkylation[18] may be based on intermediates not associated with the basic metathesis reaction. Furthermore, all WCl_6-based catalysts are either wholly (e.g., $WCl_6 + 2Li$-n-C_4H_9) or partially heterogeneous,[5,9] and, accordingly, activity and selectivity could be sensitive to the catalyst recipe and to actual experimental conditions. Finally, we note that the rate of catalyst production from the various WCl_6-based recipes varies substantially: catalyst quickly forms and dies in the $WCl_6 + C_2H_5OH + 4C_2H_5AlCl_2$ system[1,9,19] whereas in the $WCl_6 + Zn(CH_3)_2$ system[9] an insoluble, active catalyst is slowly generated over at least a 24-h period.[20] Therefore, we do not believe that an objective interpretation of the variability in "product ratios" from the terminal olefins with catalyst recipe composition[21] can be advanced at this point.

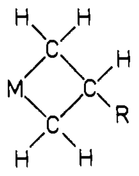
Dominance of nonproductive or degenerate metathesis in the reaction of terminal olefins with these WCl_6-based catalysts is a significant result that bears on intimate stereochemical details of the reaction intermediates. In the carbene chain hypothesis, two critical intermediates are the coordinated carbene and metallocyclobutane species which are illustrated in abbreviated forms **3** through **8** for the possible variants in a terminal olefin system. If the substituted carbene **3** is favored over the simple methylene complex **4** then Scheme II, that leads selectively to nonproductive metathesis, can be justified. This was the basis of our original speculation[1] and Casey, Tuinstra, and Saemen[22] employ a similar reasoning to account for olefin product distributions in reactions of $W(CO)_5C(C_6H_4CH_3)_2$ with terminal olefins. Alkyl substitution should stabilize a coordinated carbene but there are as yet no theoretical or experimental[23] quantitative comparisons of M-CH_2 vs. M-CHR complexes. If both carbenes **3** and **4** have nearly equal probabilities of formation in the terminal olefin metathesis reaction, then electronic and/or steric factors must favor metallocycle **5** over **6** and **7** over **8** to explain the predominance of nonproductive metathesis observed experimentally. No consistent set of electronic or steric arguments seems to be available to generate the required set of favored metallocycles (**5** and **8**).[24] Synthesis of specific tungstacyclobutanes at low temperatures followed by a study of the thermolytic products should resolve such stability[25] issues;[26] we are attempting synthesis of these metallocycles.

$M{-}CHR$

3

$M{-}CH_2$

4



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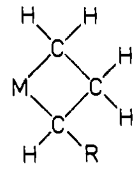

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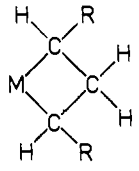

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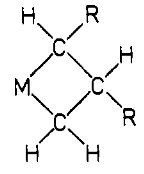

8

Acknowledgment. We gratefully acknowledge support of this research by the National Science Foundation and the

constructive comments of Professor C. P. Casey and Dr. N. Calderon especially with respect to metallocycle intermediates.

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(1) E. L. Muetterties, *Inorg. Chem.*, **14**, 951 (1975).
(2) (a) G. C. Bailey, *Catal. Rev.*, **3**, 37 (1969); (b) M. L. Khidekel, A. D. Shebaldova, and I. V. Kalechits, *Russ. Chem. Rev.*, **40**, 669 (1971); (c) R. L. Banks, *Top. Curr Chem.*, **25**, 39 (1972); (d) W. N. Hughes, *Organomet. Chem. Synth.*, 1, 341 (1972); (e) J. C. Mol and J. A. Moulijn, *Adv. Catal.*, **24**, 131 (1975); (f) R. J. Haines and G. J. Leigh, *Chem. Soc. Rev.*, **4**, 155 (1975); (g) N. Calderon, *Acc. Chem. Res.*, **5**, 127 (1972); (h) W. B. Hughes, *Chem Technol.*, 486 (1975).
(3) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **96**, 7808 (1974).
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(6) J. L. Herrisson and Y. Chauvin, *Makromol. Chem.*, **141**, 161 (1970).
(7) R. Shrock, *J. Am. Chem. Soc.*, **97**, 6577 (1975).
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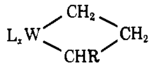
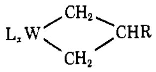
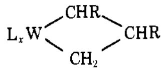
(9) E. L. Muetterties and M. A. Busch, *J. Chem. Soc., Chem. Commun.*, 754 (1974).
(10) J. Wang and H. R. Menapace, *J. Org. Chem.*, **33**, 3794 (1968).
(11) N. Calderon, E. A. Ofstead, and W. A. Judy, *J. Polym. Sci., Part A-1*, **5**, 2209 (1967).
(12) The heterogeneity (or homogeneity) of these aluminum based catalysts *is* as we originally reported as yet not established. We still consistently find the formation of solids in the interaction of $\mathrm{C_2H_5AlCl_2}$ with $\mathrm{WCl_6}$ *in the presence of olefin* (presence or absence of alcohol). R. Wolovsky and Z. Nir (*J. Chem. Soc., Chem. Commun.*, 302 (1975)) not only misinterpreted our[9] earlier results and conclusions but provided insufficient experimental details about their experiments. We do find that *inattention* to exclusion of oxygen impurities greatly affects not only activity but also *apparent* homogeneity of the $\mathrm{C_2H_5AlCl_2\text{-}WCl_6}$ catalyst (to be submitted for publication shortly). More recently, J. M. Basset, J. L. Bilhou, R. Mutin, and A. Theolier, *J. Am. Chem. Soc.*, **97**, 7376 (1975), claim a steric test for a distinction between homogeneous and heterogeneous metathesis catalysts. Among the homogeneous catalysts listed by them is the $\mathrm{Li(}n\mathrm{\text{-}C_4H_9)\text{-}WCl_6}$ reagent set which is wholly and unequivocally heterogenous;[5,9] the insolubility of this catalyst is not controversial as cited by these authors. Hence, the conclusion presented by these authors must be substantially revised.
(13) N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and D. W. Scott, *J. Am. Chem. Soc.*, **90**, 4133 (1968).
(14) N. Calderon, personal communication. Also now see J. W. Kelly and N. Calderon, *J. Macromol. Sci., Chem.*, **A9** (6), 911 (1975).
(15) The compounds were identified by GC-MS but the deuterium positions were not unambiguously determined. Nevertheless the cited isomers are the only plausible ones in view of the other olefins produced in the reaction.
(16) Note, however, that there are inherent experimental difficulties in the determination of both the equilibration time and the nonproductive:productive metathesis ratio. Over extended time periods (>24 h) as were used in these trials, evaporation of volatile components is a significant problem, especially for low boiling olefins as were used here (e.g., 1-pentene boils at 30°). Comparisons among the nonproductive:productive metathesis ratios for different catalysts were all made after 24-h reaction time and so should be valid, assuming reasonable reproducibility of experimental conditions. The determination of equilibration time for $\mathrm{CH_2\text{-}CD_2}$ exchange will be less exact, but this is not a crucial point for the arguments presented.
(17) There may be a family of metathesis catalysts and it may be imprecise to speak of *a* metathesis reaction mechanism at least in stereochemical detail.
(18) In aluminum alkyl-$\mathrm{WCl_6}$ systems, high catalyst concentrations and high Al/W ratios promote the alkylation reaction. Variations in the metal alkyl/$\mathrm{WCl_6}$ ratios can lead to significant rates of olefin isomerization or oligomerization.
(19) Catalyst lifetime in the $\mathrm{WCl_6 + 4C_2H_5AlCl_2 + C_2H_5OH}$ system is ca. 30 min at 25°.
(20) Possibly more than one catalytically active species is produced from these recipes. Each could have a distinguishable metathesis chemistry. Furthermore, each could have a different lifetime. In this case, the rate of catalyst production would become an important experimental variable.
(21) In our own hands, we find sufficient variation (especially in activity) of a catalyst recipe on nearly a day-to-day basis that quantitative comparisons are really quite difficult (see particularly the comments in ref 9).
(22) C. P. Casey private communication; C. P. Casey, H. E. Tuinstra, and M. Saemen, *J. Am. Chem. Soc.*, **98**, 608 (1976).
(23) Since Shrock[7] has now succeeded in preparing both $\mathrm{CH_2}$ and CHR carbene–tantalum complexes, an experimental comparison of stabilities in these two types of carbene complexes may be at hand.
(24) For example, steric factors should favor **5** over **6** but not 7 over **8**. Electronic factors might place **7** as the most favorable metallocycle in which case **6** should be favored over **5**.
(25) The term stability is used here in a relative sense. Obviously *high* stabilities in carbene or metallocyclobutane complexes would not be a desirable feature in a catalytic metathesis system. Very high stabilities are found in metalloidocyclobutanes For example, the decomposition of $\mathrm{H_2Si}$ to ethylene and $\mathrm{[H_2Si{=}CH_2]}$ is effected at 560°. C. M. Golino, R. D. Bush, and L. H. Sommer, *J. Am. Chem. Soc.*, **97**, 7371 (1975).
(26) If the stabilities of the carbene species **3** and **4** do, in fact, determine the stereochemical results in terminal olefin metathesis then, A


A

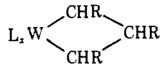
should yield primarily ethylene as should B


B

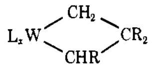
via $\mathrm{L_xW(CH_2)(\eta^2\text{-}CH_2{=}CHR)}$[27] and A intermediates, and, in the complimentary set, C


C

and D


D

should both yield primarily $\mathrm{RCH{=}CH_2}$. A metallocycle like E


E

should largely yield $\mathrm{RCH{=}CH_2}$ through an $\mathrm{L_xW(CHR)(\eta^2\text{-}R_2C{=}CH_2)}$ intermediate. If, however, RCH and $\mathrm{CH_2}$ tungsten carbene complexes have nearly identical stabilities then the expected initial products would be nearly equal amounts of $\mathrm{C_2H_4}$ and $\mathrm{RCH{=}CH_2}$ from A, $\mathrm{RCH{=}CHR}$ and $\mathrm{RCH{=}CH_2}$ from C, $\mathrm{RCH{=}CHR}$ and $\mathrm{R_2C{=}CHR}$ from E, and only $\mathrm{RCH{=}CH_2}$ from B and D.
(27) There are certain obvious assumptions here about relative rates of metallocyclobutane ring opening-olefin expulsion and rearrangement.

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Prostaglandins. I. Direct Synthesis of Optically Active Corey-Intermediate from (*S*)-(−)-Malic Acid

Sir:

Previously reported[1] syntheses of natural prostaglandins such as $\mathrm{PGF_{2\alpha}}$ (I) are based essentially on racemic starting materials and depend on the resolution of some intermediate[2,3] with the usual losses associated with such a process.

Other disadvantages of established synthetic methods are, in many cases, the numerous and/or involved steps and the use of complicated reagents, difficult to employ in large-scale work. These problems prompted us to search for alternate synthetic procedures which would avoid these hardships. In this communication, we present a new method for the direct synthesis, from (*S*)-(−)-malic acid, of the optically active form of an intermediate (II), a type of compound originally prepared by Corey et al.[4,14] We chose this goal since all of the known prostaglandins as well as numerous analogues may be synthesized[5] from this or closely related compounds.

Treatment of (*S*)-(−)-malic acid with acetyl chloride afforded[6] (*S*)-(−)-2-acetoxysuccinic anhydride (IIIa) which when heated under reflux with dichloromethyl ether in the presence of zinc chloride catalyst led to the corresponding succinyl chloride IIIb,[7,8] bp 75-80° (0.05 mmHg), $[\alpha]^{25°}\mathrm{D}$ −10 ($\mathrm{CHCl_3}$; *c*, 1.0%), in 80% yield. When 5 equiv of the dianion of methyl hydrogen malonate (derived from methyl hydrogen malonate and isopropyl magnesium bromide according to Ireland and Marshall[9]) was treated with this acid chloride at 0° in tetrahydrofuran solution, the product,