A Stereochemical Study of Metathesis and Cis–Trans Isomerization of 2-Pentenes

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Abstract: A stereochemical approach of metathesis of *cis-* and *trans-*2-pentene has been carried out with several precursor complexes of tungsten. A mechanism of coordination of the internal olefin on the two different metallocarbene moieties is proposed. It accounts for the competitive cis–trans isomerization or formal metathesis of the starting olefin. The mechanism is based on kinetic data related to the respective rates of eight elementary steps occurring at low conversion in metathesis of *cis*-2-pentene. Stereochemistry of metathesis of trans olefins has also been studied: trans olefins do not seem to be able to produce the metallocarbene responsible for the propagation, whereas cis internal olefins or α olefins can do it. The stereoselectivity observed is higher for trans olefins than for cis olefins; they can be explained on the basis of steric repulsion between the R group of the olefin and the bulky ligand coordinated to tungsten or on the basis of stability of various configurations of metallocyclobutanes. A kinetic model derived from the proposed mechanism accounts for the linear relationship observed between trans/cis C_4 or C_6 vs. trans/cis C_5 at low conversion.

Geometric isomerization of internal acyclic olefins was observed in the early works related to metathesis reaction.[1] Various stereochemical studies seem to indicate that this geometric isomerization proceeds according to a metathetic mechanism.[1-4] However, no systematic kinetic study has been performed concerning the respective kinetics of cis–trans isomerization and metathesis reaction.

A stereochemical investigation of metathesis was therefore undertaken with the following guideline: if cis–trans isomerization of the starting olefin is a probable alternative to metathesis, there must be a simple kinetic relation between the respective rates of both reactions related to the probability of coordination of the olefin to the active catalyst in such a way that it will result either in metathesis or in geometric isomerization.

In this paper, the determination of various stereoselectivities as a function of the nature of the geometric isomers of the starting olefins has been used as a probe to go deeper into the molecular approach of this reaction.

Experimental Section

Materials. Zerovalent complexes of tungsten $W(CO)_5L$ ($L = P(C_6H_5)_3$, $P(OC_6H_5)_3$, $P(n\text{-}C_4H_9)_3$, $NH_2C_6H_{11}$, pyridine), $W(CO)_4L_2$ (L_2 = diphos, en) were obtained by mixing stochiometric amounts of $W(CO)_6$ and the corresponding ligand in a sealed tube, according to a procedure already described.[5] $W(CO)_3$arene was purchased from Chemical Corp. All zerovalent complexes were purified by crystallization except for $W(CO)_5\,P(n\text{-}C_4H_9)_3$, which was purified according to Angelici.[6] WCl_6 was purified by careful sublimation.[7]

$C_2H_5AlCl_2$ was supplied from the Ethyl Corp. It was purified by vacuum distillation, diluted in anhydrous chlorobenzene, and stored under argon.

Chlorobenzene was a commercial Rhône-Poulenc grade. It was distilled twice from P_2O_5 under argon. It was stored under argon.

cis-2-Pentene was supplied from Fluka. It had a purity of 96.6% with 3.4% of trans isomer. It was distilled over Na and stored under argon.

trans-2-Pentene was supplied from Fluka. It had a purity of 99% with less than 0.5% of cis isomer. It was distilled under vacuum and stored under argon.

All the gases used (argon and oxygen) were dehydrated over molecular sieves 5A.

2. Apparatus and Procedure for Kinetics Experiments. The apparatus used for kinetics experiments included a batch reactor in glass with valves allowing argon purges, evacuation, and introduction of the various reagents. Various gases syringes as well as burets allowed given amounts of pentene, O_2, alkylaluminum, or solvent (chlorobenzene) to be introduced into the reactor. A sampling valve was connected to the reactor in order to analyze the gaseous phase or liquid phase at any time of the reaction.

Analysis of the reagents, mainly butenes, pentenes, and hexenes, was carried out with a flame ionization chromatograph.

In all experiments where no further details are given, the catalytic system employed was $W(CO)_5P(C_6H_5)_3$, $C_2H_5AlCl_2$, O_2 under the following conditions: 4×10^{-4} mol of $W(CO)_5P(C_6H_5)_3$ in 60 mL of chlorobenzene, $Al/W = 4$, $O_2/Al = 1.5$, and olefin/W = 100.

Results and Discussion

1. Proposed Mechanism for Cis–Trans Isomerization and Metathesis. Recent studies seem to indicate that olefin metathesis obeys a one-carbene exchange mechanism[8-13] initially proposed by Chauvin on kinetic grounds[8] as well as on model reactions.[13] According to this mechanism an olefin coordinated to a metallocarbene moiety goes through a four-center transition state to form a new olefin and a new metallocarbene.

We propose here a stereochemical process of coordination of the olefin on the metallocarbene moiety which is derived from the mechanism of Chauvin[8] and that we try to justify in this paper (Figure 1).

In this model we have assumed that the carbon atom of the coordinated carbene has a sp^2 character with a bond order greater than one and probably two as it has been shown with the first methylene carbene tantalum complex isolated by Schrock.[14] In this case the double bond between tantalum and the methylene group results in a rigid conformation with a high barrier to rotation as determined by NMR spectroscopy.[15]

If such is the case in metathesis there is a possible interaction between the empty p_z orbital of the coordinated carbene and a π bonding orbital of the coordinated olefin which can justify the above geometry of approach.

Rather than assuming a free rotation of the coordinated carbene simultaneously with the rotation of the coordinated olefin,[16] we have assumed therefore that the stereochemistry was only determined by the geometry of approach of the olefin.

Let us consider metathesis of *cis*-2-pentene and let us assume the equally probable formation of two metallocarbene moieties: $W{=}CHCH_3$ ($W{=}C_2$) and $W{=}CHCH_2CH_3$ ($W{=}C_3$). There are four possibilities of coordination of the starting olefin for each carbene–tungsten moiety (Figure 2).

Depending on the type of coordination of *cis*-2-pentene to one or the other carbene, one obtains (a) cis and trans isomers of the products of metathesis, 2-butenes and 3-hexenes, respectively, for the pairs of "productive" reactions 1c–2c and 7c–8c; (b) cis and trans isomers of the starting olefin, 2-pen-

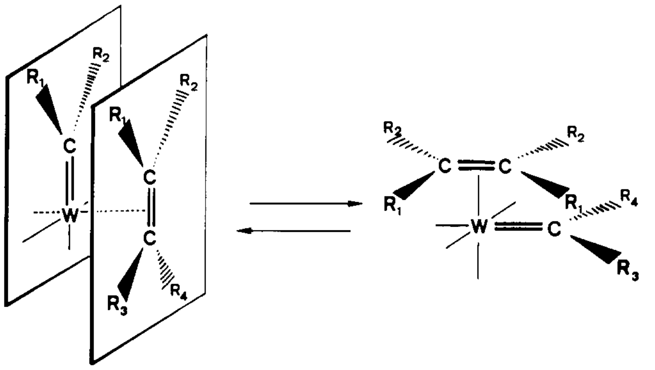


Figure 1.

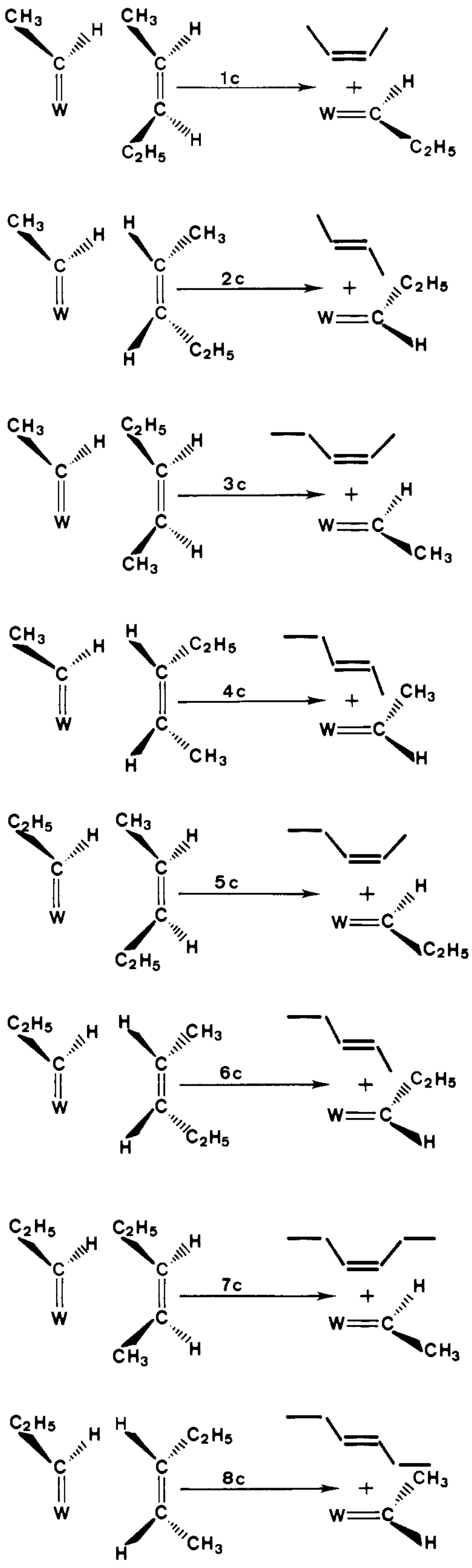


Figure 2.

tenes for the products of "regenerative" reactions 3c–4c and 5c–6c. In this latter case, there are regenerative reactions with retention of the cis configuration (3c and 5c) and regenerative reactions with inversion of the cis to trans configuration (4c and 6c).

Elementary steps leading to productive metathesis (1c–2c, 7c–8c) result in a change of the nature of the coordinated carbene whereas elementary steps leading to cis–trans isomerization of the starting olefin do not change the metallocarbene moiety. These eight reactions are the only ones which occur at very low conversion.

The situation becomes much more complicated at higher conversion since the products of formal metathesis and isomerization reactions can also coordinate to the two metallocarbenes and give secondary reactions of the same type as depicted above.

Thus, there are four possibilities of coordination of *cis*-2-butene and of *cis*-3-hexene (Figure 3).

In the same way, trans isomers (*trans*-2-pentene, *trans*-2-butene, and *trans*-3-hexene) can coordinate to the same two metallocarbenes according to 16 other similar elementary steps. Thus the combinated metathesis and geometric isomerizations which are found require a consideration of 32 carbene–olefin reactions. Nevertheless, in spite of the mechanistic complexity of such a system, kinetic data observed at low conversion are often of very simple form and seem to confirm the validity of the proposed mechanism.

2. Experimental Verification of the Proposed Mechanism. In order to determine whether the olefin is coordinated and/or reacts most easily in such a way that the R group of the carbene and of the olefin is in a cis or trans position, one has to consider the respective rates of reactions 2c and 1c, or 8c and 7c at very low conversion.

In a previous work[17] we have studied the stereochemistry of metathesis of *cis*-2-pentene and the ratios *trans*-2-butene/*cis*-2-butene (trans/cis C_4) and *trans*-3-hexene/*cis*-3-hexene (trans/cis C_6) were plotted vs. the ratio *trans*-2-pentene/*cis*-2-pentene (trans/cis C_5). This gave two linear relationships from which trans/cis C_4 and trans/cis C_6 ratios at 0% conversion can be deduced (Figure 4). The values obtained are respectively equal to 0.73 ± 0.05 and 0.88 ± 0.06, regardless of the nature of the catalyst in homogeneous phase. Therefore steric factors are not very important in determining the cis or trans approach of the olefin with respect to the metallocarbene or its reaction once it is coordinated; however, there is a slight preference for the cis approach.

Unless deuterated olefins are used, there is no experimental possibility of determining the trans/cis C_5 ratios corresponding to the ratios of the rate constants of reactions 4c and 3c on one hand, 6c and 5c on the other hand. However, a good estimate of the trans/cis C_5 ratios can be obtained if we take an average between the values 0.73 and 0.88 corresponding respectively to k_{2c}/k_{1c} and k_{8c}/k_{7c}. In the following we will take the calculated average of 0.81.

In order to determine whether the olefin is coordinated (and/or reacts) in one way or upside down with respect to the same metallocarbene, one has to compare the rates of reactions 1c and 3c, 2c and 4c, 5c and 7c, 6c and 8c. Since there is no simple experimental possibility of measuring k_{3c} and k_{5c}, the

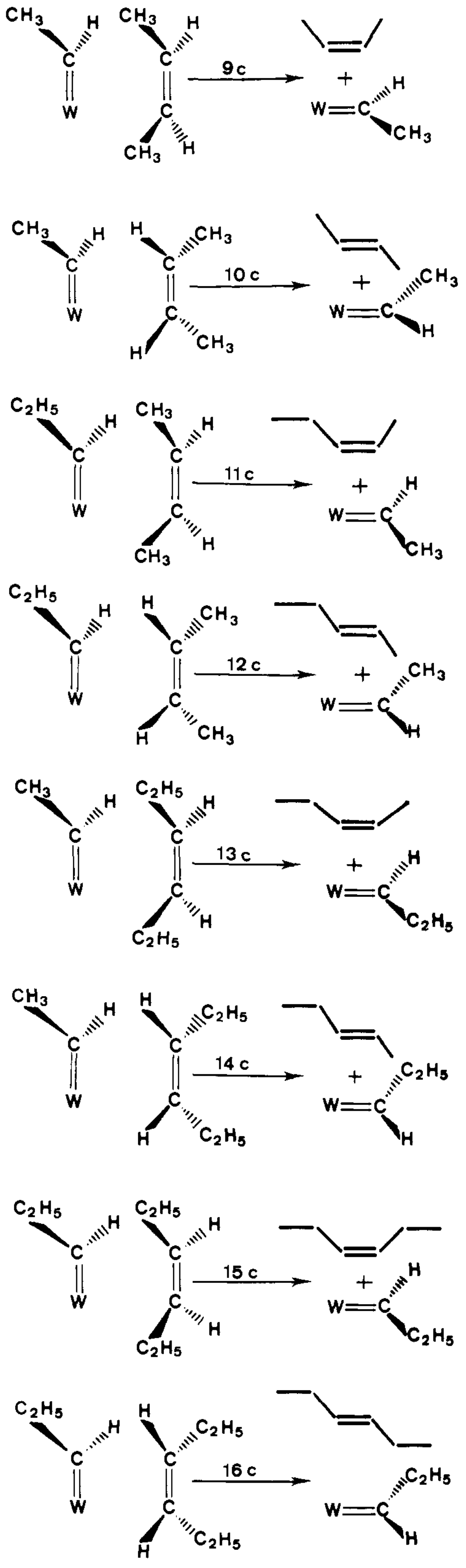


Figure 3.

only way to answer the question is to compare the rates of formation of *trans*-2-butene (k_{2c}) with the rate of formation of *trans*-2-pentene ($k_{4c} + k_{6c}$).

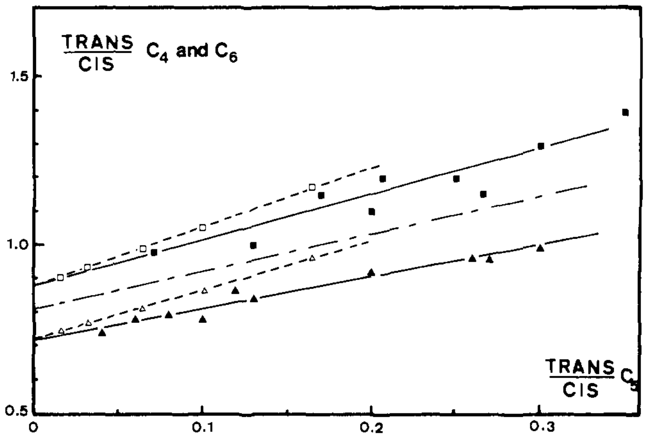


Figure 4. Ratios trans/cis C_4 and C_6 vs. ratio trans/cis C_5 in the *cis*-2-pentene metathesis: (▲) trans/cis C_4 found; (△) trans/cis C_4 calculated; (■) trans/cis C_6 found; (□) trans/cis C_6 calculated; (— - —) trans/cis C_5 estimated where cis C_5 is the *cis*-2-pentene produced only by the reactions 3c and 5c.

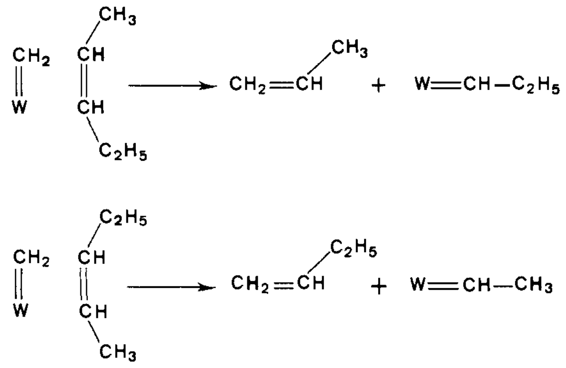


Figure 5.

To achieve this, many catalytic reactions of metathesis of *cis*-2-pentene have been performed. The activity of the various catalytic systems used has been strongly decreased by introducing the olefin a long time following the mixing of the catalytic components.[4] In Table I are reported the various rates observed for formal metathesis and cis–trans isomerization of the starting olefin for the catalytic system $W(CO)_5$-$P(C_6H_5)_3$-$C_2H_5AlCl_2$-O_2 exhibiting low initial rates of metathesis and for other different catalytic systems. It must be pointed out that with these catalytic systems, the only products observed during the catalytic reaction are the cis and trans isomers of the starting olefin as well as the cis and trans isomers of the products of formal metathesis. The extent of double bond shift is usually lower than 0.5% even at thermodynamic equilibrium. The absence of double bond isomerization suggests that a metal-hydride species which would be responsible for both double bond shift and cis–trans isomerization is probably not involved at least in the propagation step.

With $W(CO)_5P(C_6H_5)_3$ associated with $C_2H_5AlCl_2$, an average value of 2.6 ± 0.4 has been obtained for $(k_{4c} + k_{6c})/k_{2c}$ instead of the expected value of 2 if the three reactions were equally probable. A value close to 2 is also found for the other catalytic systems.

Analogously, a value of 2.5 ± 0.6 has been obtained for $(k_{3c} + k_{4c} + k_{5c} + k_{6c})/(k_{1c} + k_{2c})$ instead of the value of 2 expected for the six equally probable reactions. This indicates that certain modes of coordination are slightly preferred.

In another typical experiment, a metathesis reaction was initiated with 1-pentene (3.6×10^{-2} mol) so as to promote the formation of $W{=}CH_2$ and $W{=}CH(CH_2)_2CH_3$, the molar ratio (1-pentene)/W being equal to 90. Then *cis*-2-pentene (0.4×10^{-2} mol) was introduced 10 min later in the reaction medium. The respective amounts of propylene and 1-butene were then measured in the early stages following introduction of *cis*-2-pentene; these two α olefins are formed according to the reactions in Figure 5.

Table I. Reaction Rates[a] at Very Low Conversion[b] for the Metathesis and Isomerization Reactions of *cis*-2-Pentene

System	C_4 trans	C_4 cis	ΣC_4	C_5 trans[d]	C_5 cis[e]	ΣC_5	C_5 trans/C_4 trans	$\Sigma C_5/\Sigma C_4$
$W(CO)_5PPh_3$[c]	4.1	4.32	8.42	9.54	10.0	19.5	2.33	2.3
$W(CO)_5PPh_3$[c]	3.12	3.42	6.54	8.52	8.87	17.5	2.73	2.7
$W(CO)_5PPh_3$[c]	2.76	3.18	5.94	7.56	7.96	15.5	2.74	2.6
$W(CO)_5PPh_3$[c]	2.4	3.42	5.4	6.24	6.57	12.8	2.6	2.4
$W(CO)_5PPh_3$[c]	2.4	2.88	5.28	7.02	7.39	14.4	2.93	2.7
$W(CO)_5PPh_3$[c]	2.16	2.64	4.8	6.12	6.44	12.6	2.83	2.6
$W(CO)_5PPh_3$[c]	1.48	1.92	3.4	4.02	4.23	8.25	2.72	2.4
$W(CO)_5PPh_3$[c]	1.38	1.8	3.18	4.02	4.23	8.25	2.91	2.6
$W(CO)_5PPh_3$[c]	0.59	0.84	1.43	1.32	1.39	2.71	2.24	1.9
$W(CO)_5PPh_3$[c]	0.5	0.52	1.02	1.24	1.31	2.55	2.48	2.5
$W(CO)_5PPh_3$[c]	0.23	0.27	0.5	0.56	0.59	1.15	2.43	2.3
$W(CO)_5PPh_3$[c]	0.24	0.26	0.5	0.67	0.71	1.38	2.79	2.7
							Av 2.6 ± 0.4	2.5 ± 0.6
$W(CO)_5P(Bu)_3$[c]	11.7	12.1	23.8	26.3	23.9[f]	50.2	2.25	2.11
$W(CO)_5P(OPh)_3$[c]	0.22	0.26	0.48	0.61	0.64[e]	1.25	2.8	2.6
trans-$W(CO)_4(PPh_3)_2$[c]	0.27	0.32	0.59	0.78	0.82[e]	1.6	2.9	2.7
$WCl_6 + Sn(CH_3)_4$	0.34	0.42	0.76	1	1.05[e]	2.05	2.9	2.7
$Mo(NO)_2Cl_2(PPh_3)_2 + C_2H_5AlCl_2$	1.14	1.2	2.34	2.42	2.2[f]	4.62	2.12	2

[a] The units of all rates are 10^3 mol olefin (mol catalyst)$^{-1}$ s^{-1}. [b] At 0% conversion, we found (Figure 5) a ratio trans/cis $C_4 = 0.73$ whereas this ratio is equal to 2.8 at the thermodynamic equilibrium; in this table, all the values of trans/cis C_4 ratios are smaller than 0.96. [c] The zero-valent tungsten compounds are associated with the cocatalytic system $C_2H_5AlCl_2 + O_2$ under the conditions reported before. [d] To obtain these values, we have subtracted the initial quantity of *trans*-2-pentene in *cis*-2-pentene from the value of *trans*-2-pentene produced. [e] In this table the average value of the ratio trans/cis C_4 was found to be equal to 0.84, so we estimated in Figure 5 the corresponding value of the ratio trans/cis C_5; with the value 0.95 found, we have obtained the quantity of *cis*-2-pentene produced by 3c and 5c reactions. [f] For these two systems, the value of the ratio trans/cis C_4 is equal to 0.96; so we have taken the ratio trans/cis C_5 equal to 1.1 to calculate the *cis*-2-pentene produced by 3c and 5c reactions.

When 9.1% of the initial *cis*-2-pentene was converted, 0.014×10^{-2} mol of propylene and 0.017×10^{-2} mol of 1-butene were found in the products, corresponding to a molar ratio of propylene over 1-butene equal to 0.82.

Consequently, it seems that the mode of coordination of *cis*-2-pentene in one way or upside down with respect to a metallocarbene ($W{=}CH_2$, $W{=}CHCH_2CH_3$) does not result in a drastic change of the rate of both reactions.

The conclusion which can be drawn from all these experiments is that initial rates of cis-trans isomerization and of productive metathesis are compatible with the proposed mechanism. Besides, the fact that we observe a trans/cis ratio close to unity for C_4 and C_6 is in good agreement with the fact that the ratio isomerization rate/metathesis rate is close to two in the frame of a carbene type mechanism. In the absence of any steric effect one should obtain trans/cis C_4 = trans/cis C_6 = 1 and trans C_5/trans C_4 = 2 at very low conversion. However, this fairly good agreement does not constitute a proof in favor of the one carbene exchange mechanism.

3. Stereochemistry of Metathesis of Trans Olefins. There are only a few data in the literature[1,2,7] dealing with the reactivity and stereoselectivity of metathesis of trans isomers of internal olefins. It is generally admitted that trans olefins are less reactive than cis olefins and that the resulting stereoselectivity is also different from that observed with cis isomers.

A first experimental observation deserves to be pointed out: with the catalytic systems $W(CO)_5P(C_6H_5)_3$–$C_2H_5AlCl_2 + O_2$ and $W(CO)_3$ (mesitylene)–$C_2H_5AlCl_2 + O_2$ in the already described conditions, no catalytic activity in metathesis is observed when the starting olefin is pure *trans*-2-pentene (*trans*-2-pentene/W = 100). However, it is very hard to observe accurately this phenomenon; if the *trans*-2-pentene contains a cis or a terminal olefin even with less than 0.2%, metathesis reaction takes place after an induction period of varying length; then the reaction seems to be autocatalytic for the first minutes.

Such an observation was already mentioned by Pampus[18] in metathesis of *trans*-2-butene with the catalytic system WCl_6–CH_3AlCl_2.

The simplest explanation for this unexpected behavior would be to consider the initiation step corresponding to the first metallocarbene separately from the propagation step. Steric factors related to the nature of the geometric isomers of the starting olefin would be a key factor during the initiation period: *trans*-2-pentene alone is not able to produce the first metallocarbene, whereas a very small amount of the cis isomer can do it, and thus promotes metathesis reaction; the cis isomers thus obtained produce again the metallocarbene responsible for the propagation step. This explanation accounts thus for the autocatalytic aspects of the metathesis of trans olefins.

The strong effect of the geometric nature of the isomers on the formation of the metallocarbene moieties responsible for the propagation has been corroborated by two experiments: cross-metathesis between 1-pentene and *cis*- or *trans*-2-pentene was carried out with the catalytic system $W(CO)_5P(C_6H_5)_3$, $C_2H_5AlCl_2$, O_2. The respective distribution of the cross-metathesis products C_2H_4, C_3H_6, 1-butene, and 2-butene has been plotted vs. time in Figures 6 and 7.

Comparison between Figures 6 and 7 shows the strong influence of the nature of the geometric isomers of 2-pentene on the product distribution at low conversion.

With *cis*-2-pentene, self-metathesis leading to 2-butene occurs to a significant extent which is in agreement with the results of Calderon and coworkers.[16] However, with *trans*-2-pentene, self-metathesis of 2-pentene leading to 2-butene does not occur initially, whereas self-metathesis of 1-pentene and cross-metathesis of *trans*-2-pentene with 1-pentene take place (Figure 7).

The only explanation for such behavior is to consider that *trans*-2-pentene alone is not able to produce the two metallocarbene moieties, $W{=}CHCH_3$ and $W{=}CHC_2H_5$, whereas *cis*-2-pentene can. A similar experimental fact was also ob-

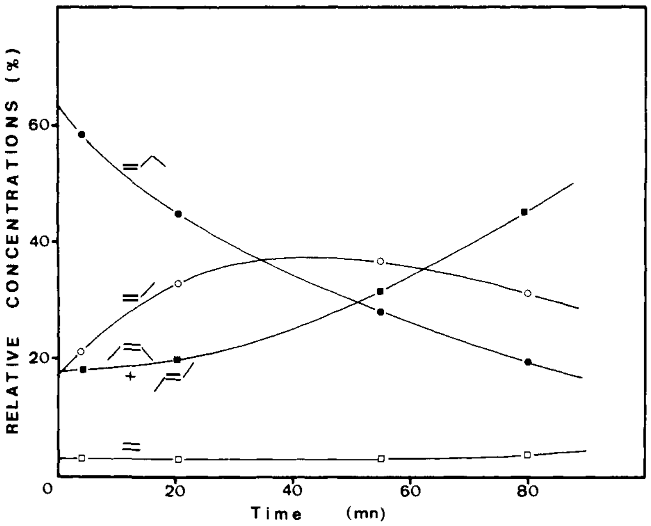


Figure 6. Cross metathesis of 1-pentene and *cis*-2-pentene: 1-pentene/W = *cis*-2-pentene/W = 100.

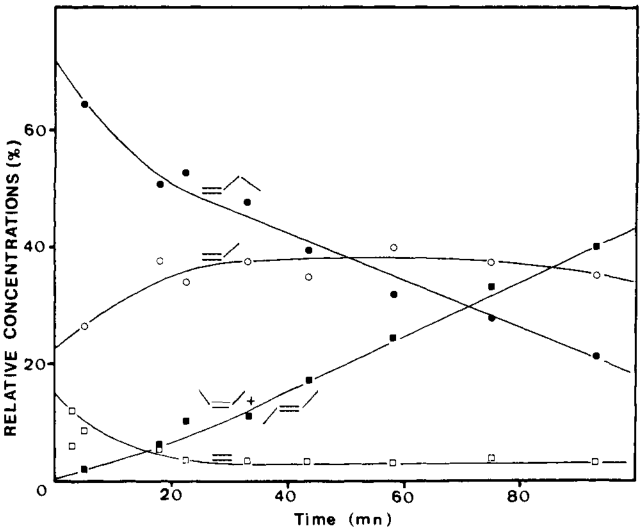


Figure 7. Cross metathesis of 1-pentene and *trans*-2-pentene: 1-pentene/W = *trans*-2-pentene/W = 100.

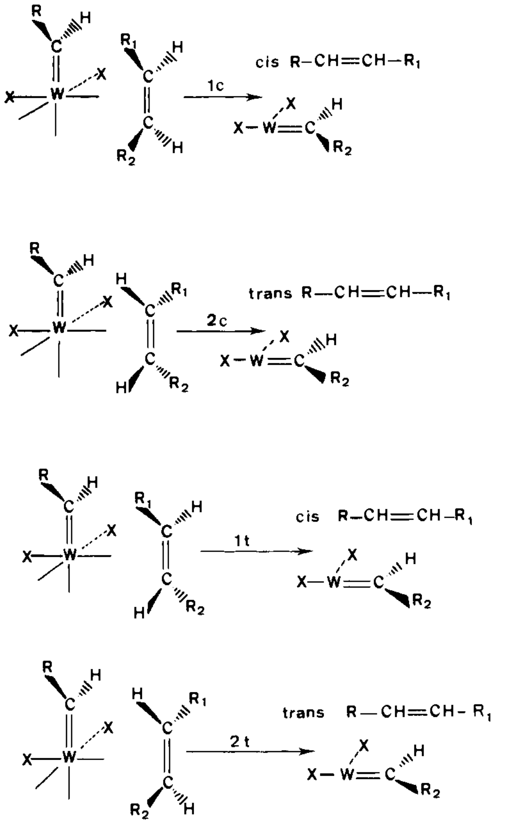


Figure 8. Top: Approach of a cis olefin. Bottom: Approach of a trans olefin.

served by Chevalier et al.[19] in the cross-metathesis between allylbenzene and *trans*-1-phenyl-2-butene with the catalytic system $Mo(NO)_2Cl_2(P(C_6H_5)_3)_2$-$C_2H_5AlCl_2$.

As a conclusion to the above experiments, it seems that steric factors are of primary importance in the formation of the first active center responsible for the propagation step in the chain reaction; α olefins or cis internal olefins with a good accessibility of the double bond lead most easily to the tungsten-carbene moiety.

Another aspect of the metathesis of *trans*-2-pentene is related to the corresponding stereoselectivity at 0% conversion. Due to the fact that *trans*-2-pentene alone cannot initiate metathesis, we have performed metathesis of *trans*-2-pentene containing 1% of 1-hexene (4×10^{-4} mol of hexene). (In these conditions formal metathesis of *trans*-2-pentene has a rate which is slightly smaller than that obtained with *cis*-2-pentene.) The value obtained in this case for trans/cis ratio of C_4 is equal to 2.0 and indicates a greater stereoselectivity with *trans*-2-pentene than that observed with *cis*-2-pentene. We are going to interpret this fact as arising from a "one-carbene exchange mechanism."

4. Interpretation of the Observed Stereoselectivity. It is necessary to recall here the various selectivities observed in metathesis of *cis*- or *trans*-2-pentene. When starting from *cis*-2-pentene, cis isomers are slightly favored in the products (trans/cis C_4 = 0.73, trans/cis C_6 = 0.88). If the complex is deposited on a surface the cis isomers are much more favored (trans/cis C_4 = 0.37).[17] When starting from *trans*-2-pentene, trans isomers are favored (trans/cis C_4 = 2.0).

It is possible to explain the observed stereoselectivities in terms of the steric effect for the coordination of the olefin assuming that complexation is rate determining or in terms of the stability of the metallocyclobutane if such a complex is a real intermediate.

4a. For the first alternative, it is possible to formulate several hypotheses concerning the steric factors which govern the approach of the olefin to the metallocarbene moiety. We have summarized in Figure 8 two possible approaches of a cis olefin and of a trans olefin to the tungsten. In such a model two kinds of steric interaction may occur: (a) between the alkyl group of the coordinated carbene and that of the olefin which approaches in a cis position (reactions 1c and 1t) or in a trans position (reaction 2c and 2t); (b) between the metal and/or its ligands and the alkyl groups of the olefin.

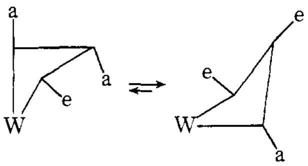
Since reaction 1c is slightly favored compared with reaction 2c (trans/cis C_4 = 0.73) and reaction 7c compared with reaction 8c (trans/cis C_6 = 0.88) it is logical to assume that the major steric effects are due to the ligands still coordinated to the metal and not to the R group of the coordinated carbene. If the latter case were true one would expect the olefin to coordinate preferentially according to reaction 2c. This conclusion is corroborated by two different experimental observations related to metathesis of *cis*-2-pentene: (a) the higher stereoselectivity in favor of cis isomers with supported complexes for which the surface can be considered as a bulky ligand;[17] (b) the higher stereoselectivity in favor of cis isomers with homogeneous catalytic systems derived from tungsten having bromide ligands instead of chloride ligands.[20]

It is arbitrary at the present time to propose a model of the coordination sphere of tungsten in metathesis of olefins. A useful approach to the explanation of the observed stereoselectivity would be to consider a tungsten having one coordinated carbene with two ligands X. It has recently been shown that $W(CO)_4Cl_2$ is one of the metathesis catalysts which does not require any cocatalyst[24] so that a tungsten (II) active species is not unreasonable; concerning the rest of the coordination sphere, there is no information to decide whether or not tungsten is highly unsaturated or possesses other ligands which would not influence the reaction stereochemistry (oxo ligands[25]). Assuming an octahedral symmetry the R group of the coordinated carbene must be in trans position with respect to the bulky ligand X coordinated to tungsten (Figure 8). We have admitted in Figure 8 that after the carbene exchange step, the produced carbene would attain a stable configuration with its R group in trans position with respect to at least one ligand X.

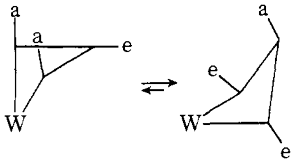
Thus if we consider that the steric effect of X is the predominant factor, the approach of a cis olefin according to 1c will be slightly favored compared with 2c. If one increases the size of one ligand X, for example, in the case of the surface, the approach according to 1c will be much more favored. In the case of a trans olefin it is logical to observe that the approach according to 2t will be favored. In this case the model also accounts for the fact that stereoselectivity observed with trans isomers is higher than with cis isomers in our case as well as with molybdenum complexes.[2] In fact the two R groups of the coordinating olefin are away from both the ligands X and from the R group of the coordinated carbene.

The model also accounts for the fact that isomerization of *cis*-2-pentene to *trans*-2-pentene is preferred over formal metathesis ($(k_{4c} + k_{6c})/k_{2c} = 2.6$ instead of 2). In effect, if we assume that the steric effect of X is the predominant factor, the approach of *cis*-2-pentene according to reaction 4c will be favored compared with reaction 2c, whereas reaction 2c and 6c should have comparable rates. Therefore $(k_{4c} + k_{6c})/k_{2c}$ should be higher than 2.

4b. The second alternative would be to consider only the stability of a tungstacyclobutane intermediate. In this case, the cis or trans approach of a cis olefin will result in two different metallocyclobutanes:

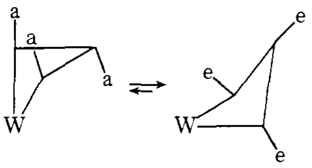


I
trans approach

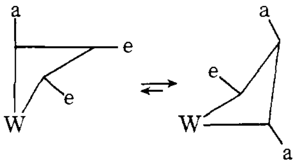


II
cis approach

In the same way the cis or trans approach of a trans olefin will result in two other different metallocyclobutanes:



IV
trans approach



III
cis approach

Such considerations may account for the trans stereoselectivity with trans olefins since IV is more stable than III but no definite conclusion can be drawn for cis olefins. However, such a consideration would not explain the steric effect of a bulky ligand such as a surface or a halogen. Also it does not explain the respective rates of cis-trans isomerization and metathesis. In fact more data are necessary before reaching a definite decision between the two alternatives.

5. Kinetic Model Derived from the Proposed Mechanism. In the mechanism of coordination of the olefin proposed, cis-trans isomerization of the starting olefin is competitive with productive metathesis. Thus it should be possible to derive a mathematical model which accounts for the linear relationship observed between trans/cis C_4 and C_6 vs. trans/cis C_5.

Let us consider the 32 elementary reactions occurring during metathesis of *cis*-2-pentene. We will refer to as "ic" and "it" the reactions occurring with a cis or a trans olefin and which result on the same product olefin, and K_4, K_5, and K_6 the cis-trans equilibrium constants at 25 °C for respectively 2-butene, 2-pentene, and 3-hexene.

The following rate equations may be derived from the proposed mechanism:

$$\begin{aligned}\partial[\text{trans } C_4]/\partial t &= k_{2c}[W{=}C_2][\text{cis } C_5] \\ &\quad + k_{2t}[W{=}C_2][\text{trans } C_5] + k_{10c}[W{=}C_2][\text{cis } C_4] \\ &\quad - k_{9t}[W{=}C_2][\text{trans } C_4] - k_{11t}[W{=}C_3][\text{trans } C_4] \\ &\quad - k_{12t}[W{=}C_3][\text{trans } C_4] \end{aligned} \tag{V.1}$$

We will assume in the following that $[W{=}C_2] = [W{=}C_3]$. Thus

$$\begin{aligned}\partial[\text{trans } C_4]/\partial t &= [\text{carbene}]\{k_{2c}[\text{cis } C_5] + k_{2t}[\text{trans } C_5] \\ &\quad + k_{10c}[\text{cis } C_4] - (k_{9t} + k_{11t} + k_{12t})[\text{trans } C_4]\}\end{aligned} \tag{V.2}$$

Likewise

$$\begin{aligned}\partial[\text{cis } C_4]/\partial t &= [\text{carbene}]\{k_{1c}[\text{cis } C_5] + k_{1t}[\text{trans } C_5] \\ &\quad - (k_{10c} + k_{11c} + k_{12c})[\text{cis } C_4] + k_{9t}[\text{trans } C_4]\}\end{aligned} \tag{V.3}$$

$$\begin{aligned}\partial[\text{trans } C_6]/\partial t &= [\text{carbene}]\{k_{8c}[\text{cis } C_5] + k_{8t}[\text{trans } C_5] \\ &\quad + k_{16c}[\text{cis } C_6] - (k_{13t} + k_{14t} + k_{15t})[\text{trans } C_6]\}\end{aligned} \tag{V.4}$$

$$\begin{aligned}\partial[\text{cis } C_6]/\partial t &= [\text{carbene}]\{k_{7c}[\text{cis } C_5] + k_{7t}[\text{trans } C_5] \\ &\quad - (k_{13c} + k_{14c} + k_{16c})[\textit{cis } C_6] + k_{15t}[\text{trans } C_6]\}\end{aligned} \tag{V.5}$$

$$\begin{aligned}\partial[\text{trans } C_5]/\partial t &= [\text{carbene}]\{(k_{4c} + k_{6c})[\text{cis } C_5] \\ &\quad - (k_{1t} + k_{2t} + k_{3t} + k_{5t} + k_{7t} + k_{8t})[\text{trans } C_5] \\ &\quad + k_{12c}[\text{cis } C_4] + k_{12t}[\text{trans } C_4] \\ &\quad + k_{14c}[\text{cis } C_6] + k_{14t}[\text{trans } C_6]\}\end{aligned} \tag{V.6}$$

At thermodynamics equilibrium, all differentials are equal to zero; in particular

$$\frac{\partial[\text{cis } C_4]}{\partial t} + \frac{\partial[\text{trans } C_4]}{\partial t} = 0 \tag{V.7}$$

From eq V.7, it is possible to derive eq V.8 in view of thermodynamic equilibria of the different isomers as well as of thermodynamic equilibria of metathesis ($[\text{cis } C_4] + [\text{trans } C_4] = \frac{1}{2}([\text{cis } C_5] + [\text{trans } C_5])$).

$$\frac{k_{1c} + k_{2c} + (k_{1t} + k_{2t})k_5}{k_{11c} + k_{12c} + (k_{11t} + k_{12t})K_4} = \frac{1 + K_5}{2(1 + K_4)} \tag{V.8}$$

The above equations cannot be solved unless a few hypotheses are made concerning the relative rates of some elementary steps. Since one cannot distinguish between the two probabilities of coordination of a given symmetric olefin in one way or upside down with respect to the same metallocarbene moiety, it is logical to assume that

$$k_{11c} + k_{12c} = 2(k_{1c} + k_{2c}) \tag{V.9}$$

$$k_{11t} + k_{12t} = 2(k_{1t} + k_{2t}) \tag{V.10}$$

More generally we will admit, for $0 \leqslant i \leqslant 7$:

$$k_{(i+9)c} = 2k_{(i+1)c} \tag{V.11}$$

$$k_{(i+9)t} = 2k_{(i+1)t} \tag{V.12}$$

Combination of V.11 and V.12 with V.8 gives the general equation, for $0 \leqslant i \leqslant 7$:

$$k_{(2i+1)c} + k_{(2i+2)c} = k_{(2i+1)t} + k_{(2i+2)t} \tag{V.13}$$

Table II. Relative Values of the Rate Constants of the Eight Primary Reactions Occurring in *cis*-2-Pentene Metathesis

Isomer formed	Product formed			
	C_4	$C_5{}^a$	$C_5{}^a$	C_6
Cis	$k_{1c} = 1$	$k_{3c} = 0.96$	$k_{5c} = 0.96$	$k_{7c} = 0.92$
Trans	$k_{2c} = 0.73$	$k_{4c} = 0.77$	$k_{6c} = 0.77$	$k_{8c} = 0.81$

[a] Estimated values.

Table III. α Values Corresponding to the Maximum of *cis*-2-Butene Concentration during Metathesis of *cis*-2-Pentene

Expt	1	2	3	4	5	6
α	0.38	0.32	0.34	0.36	0.38	0.37
Av			0.36			

Table IV

α	Conversion, %	Trans/cis C_4	Trans/cis C_5	Trans/cis C_6
0	0	0.73	0	0.88
0.01	1.2	0.75	0.016	0.91
0.02	2.3	0.77	0.032	0.93
0.04	4.5	0.82	0.064	0.99
0.06	6.6	0.87	0.102	1.06
0.09	9.6	0.96	0.164	1.18

As a consequence of eq V.11, it is possible to deduce the rate constant of any reaction involving the coordination of cis olefin from the relative values of the rate constants of the eight elementary steps occurring with *cis*-2-pentene at very low conversion (Table II).

Such a calculation can also be made from eq V.12 and V.13 for trans olefins. Unfortunately there are only a few data concerning stereoselectivity of metathesis of trans olefins. We will assume as a good approximation that, for $0 \leqslant i \leqslant 7$:

$$k_{(2i+2)t}/k_{(2i+1)t} = 2 \qquad \text{(V14)}$$

which is the experimental value obtained for $i = 0$. It is then possible to deduce from the rate constants the mathematical law relating the trans/cis ratios of C_4 and C_6 vs. the trans/cis ratio of C_5.

Let us take the variable α = cis C_4/cis C_5; for low conversion, that is, for low values of α, we shall take the experimental values trans C_5/trans C_4 = 2.6, trans C_4/cis C_4 = 0.73, trans C_6/cis C_6 = 0.88, and the estimated value trans C_5/cis C_5 = 0.81. Incorporating these values in V.2 and V.3 one obtains

$$\begin{aligned}\partial[\text{trans } C_4]/\partial t = {} & [\text{carbene}][\text{cis } C_5]\{k_{2c} \\ & + \alpha[(2.6 \times 0.73 \times k_{2t} + k_{10c}) \\ & - 0.73(k_{9t} + k_{11t} + k_{12t})]\} \qquad \text{(V.15)}\end{aligned}$$

$$\partial[\text{trans } C_4]/\partial t = [\text{carbene}][\text{cis } C_5](0.73 - 0.27\alpha) \qquad \text{(V.16)}$$

$$\partial[\text{cis } C_4]/\partial t = [\text{carbene}][\text{cis } C_5](1 - 2.97\alpha) \qquad \text{(V.17)}$$

A maximum value for [cis C_4] is expected from eq V.17 when $\alpha = 1/2.97 = 0.34$, in agreement with the kinetics curves obtained in the *cis*-2-pentene metathesis (Figure 9).

From many experiments we found a maximum for concentration of *cis*-2-butene for an average value of α equal to 0.36 (Table III).

Let us consider now eq V.16 and V.17; for very low values of α, that is, for low concentration, we can write

$$\frac{\text{trans } C_4}{\text{cis } C_4} = \frac{0.73 - 0.27\alpha}{1 - 2.97\alpha} \qquad \text{(V.18)}$$

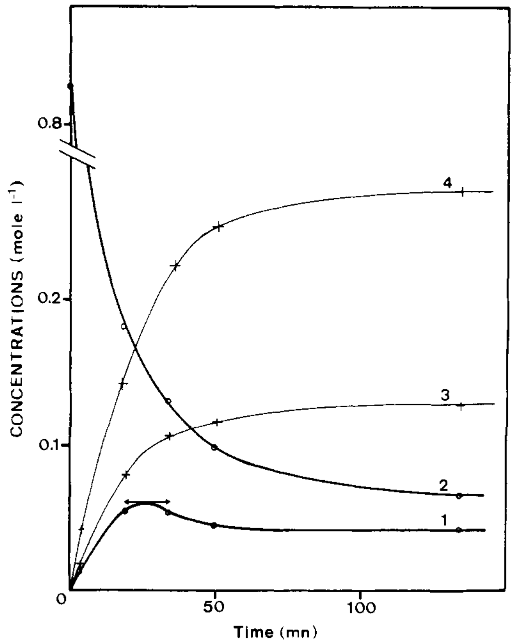


Figure 9. *cis*-2-Pentene metathesis: 1, *cis*-2-butene; 2, *cis*-2-pentene; 3, *trans*-2-butene; 4, *trans*-2-pentene. *cis*-2-pentene/W = 100.

From eq V.4 and V.5 we can deduce in the same conditions

$$\frac{\text{trans } C_6}{\text{cis } C_6} = \frac{0.81 - 0.069\alpha}{0.92 - 2.63\alpha} \qquad \text{(V.19)}$$

In the same way from eq V.6 we have

$$\frac{\text{trans } C_5}{\text{cis } C_4} = \frac{1.54 - 2.27\alpha}{1 - 2.97\alpha} \qquad \text{(V.20)}$$

$$\frac{\text{trans } C_5}{\text{cis } C_5} = \frac{1.54\alpha - 2.27\alpha^2}{1 - 2.97\alpha} \qquad \text{(V.21)}$$

We have calculated in Table IV the values of eq V.18, V.19, and V.21 for different values of α.

Upon varying α between 0 and 0.1, we have deduced the corresponding values of trans/cis C_4, trans/cis C_5, and trans/cis C_6. These calculated values deduced from the proposed mechanism have been plotted in Figure 4 in comparison with the experimental ones.

Firstly it is noteworthy that a linear relation is observed between the trans/cis ratios of C_4 and C_6 vs. the trans/cis ratio of C_5 which is in good agreement with the starting hypothesis concerning the various possibilities of coordination of the olefin.

Secondly the slope of the calculated linear relationship is fairly close to the experimental one, especially if one considers the various hypotheses that we had to make concerning some of the rate constants.

We consider that the result is a good confirmation of these different assumptions (mechanistic as well as kinetic).

Conclusion

This stereochemical approach of metathesis of internal olefin has indicated that cis–trans isomerization of any internal olefin can be considered as a particular case of metathesis, both reactions being the result of a "one-carbene exchange" mechanism.[21] The mechanism that we propose for coordination of the olefin is simply based on the fact that since the coordinated carbene has a high barrier to rotation, the stereochemistry will depend mostly on the geometry of approach of the incoming olefin.

The information that can be derived from this stereochemical study is the following. (a) In the case of internal olefins of the type $R_1CH{=}CHR_2$ for which R_1 is not very different from R_2, it seems that steric factors are more pronounced in the initiation step leading to the first metallocarbene, rather than in the propagation step. Initiation seems to require a cis olefin or an α olefin. Propagation is less sterically demanding.

(b) Concerning *cis*-2-pentene, productive metathesis and cis–trans isomerization are the results of four different types of coordination of *cis*-2-pentene on the same metallocarbene. It seems that these four types of coordination and/or reaction have about the same rate.

(c) The stereoselectivities observed with cis and trans olefin can be explained on the basis of steric repulsion between the R groups of the olefin and the bulky ligands coordinated to tungsten, or stability of various configurations of metallocyclobutanes.

Most of the conclusions drawn here are related to internal olefins for which the R groups are not significantly different. In fact various recent works by Calderon,[16] Katz,[22] and Casey[23] seem to indicate that in the case of α olefins some types of coordination (head to tail) leading to "regenerative" metathesis are much more favored than others (head to head) leading to "productive" metathesis. These results are not surprising if we consider that steric effects of alkylidene groups are in this case very different and can play a role (a) on the nature of the first metallocarbene formed during the initiation steps; (b) on the course of the chain mechanism itself where some catalytic cycles can be much more favored than others.

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Changing Views on the Mechanism of Base Catalysis in Nucleophilic Aromatic Substitution. Kinetics of Reactions of Nitroaryl Ethers with Piperidine and with *n*-Butylamine in Aqueous Dioxane

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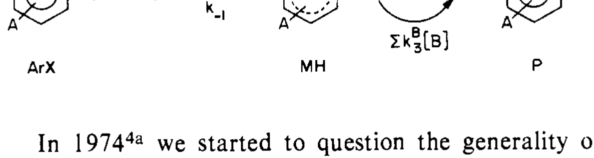
Abstract: The reactions of piperidine with 2-cyano-4-nitrophenyl phenyl ether in 10% aqueous dioxane, and of *n*-butylamine with 1-methoxy-4,7-dinitronaphthalene in 60% aqueous dioxane, are subject to general base catalysis; the reaction of *n*-butylamine with 2,4-dinitroanisole in the same solvent is probably also general base catalyzed. The reactions of piperidine with 2,4-dinitroanisole and with 1-methoxy-4,7-dinitronaphthalene in 60% aqueous dioxane are subject to specific base catalysis; the reactions of *n*-butylamine with 2-cyano-4-nitrophenyl phenyl ether and with 2,4-dinitrophenyl phenyl ether in 10% and in 60% aqueous dioxane are not subject to base catalysis. General base catalysis is shown to be a consequence of rate-limiting deprotonation of the zwitterionic intermediate complex, specific base catalysis a consequence of rapid equilibrium deprotonation of the zwitterion followed by spontaneous (noncatalyzed) leaving group expulsion. This is at variance with the hitherto generally accepted SB–GA mechanism. It is shown that the rate-limiting proton transfer mechanism is a general one in protic solvents while the SB–GA mechanism is only a significant pathway in aprotic media.

The broad mechanistic features of activated nucleophilic aromatic substitutions by amines are well established, mainly due to the work of Bunnett in the 1950s and 1960s.[1,2] The mechanism is commonly represented by eq 1.

Until recently the detailed mechanism of the base-catalyzed product-forming step(s) ($k_3{}^B$; B usually lyate ion and RR′NH) also seemed established.[1,3] It consisted of a rapid equilibrium deprotonation of MH, followed by rate-limiting, *general-acid-catalyzed* leaving group expulsion (SB–GA for specific base-general acid).



(1)

In 1974[4a] we started to question the generality of the SB–GA mechanism and suggested that, under certain cir-