tion products with CO and PPh_3 but at a much slower rate than in the preceding case. The benzyl anion, **5**, under the same conditions did not yield insertion products upon treatment with either CO or PPh_3.

References and Notes

(1) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 575 (1972); F. A. Cotton and C. M. Lukehart, *Prog. Inorg. Chem.*, **16**, 243 (1972).
(2) F. R. Kreissl, E. O. Fischer, C. G. Kreiter, and H. Fischer, *Chem. Ber.*, **106**, 1262 (1973).
(3) F. R. Kreissl and E. O. Fischer, *Chem. Ber.*, **107**, 183 (1974).
(4) J. A. Connor and E. O. Fischer, *Chem. Commun.*, 1024 (1970).
(5) E. O. Fischer and V. Kiener, *Angew. Chem., Int. Ed. Engl.*, **6**, 961 (1967).
(6) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **95**, 5833 (1973).
(7) C. P. Casey and W. R. Brunsvold, *J. Organomet. Chem.*, **77**, 345 (1974).
(8) The perfluoropropenyl and substituted acetylide pentacarbonyl anions of group 6 metals are known: W. J. Schlientz and J. K. Ruff, *J. Organomet. Chem.*, **33**, C64 (1971); *J. Chem. Soc. A*, 1139 (1971).
(9) E. W. Abel, I. S. Butler, and J. G. Reid, *J. Chem. Soc.*, 2068 (1963).
(10) Anal. Calcd for $C_{14}H_{23}NO_5W$: C, 35.84; H, 4.94; W, 39.18. Found: C, 35.70; H, 4.87; W, 38.95.
(11) One and one-half grams of the acyl compound in 20 ml of acetone was photolyzed in a Srinivasan-Griffin Photochemical Reactor at 3500 Å with a stream of nitrogen bubbling through the solution. The course of the reaction was monitored by NMR.
(12) E. O. Fischer and A. Massböl, *Angew. Chem., Int. Ed. Engl.*, **3**, 580 (1964).
(13) Anal. Calcd for $C_{19}H_{25}NO_5W$: C, 42.96; H, 4.74; W, 34.61. Found: C, 42.55; H, 4.67; W, 35.46.
(14) M. Y. Darensbourg and D. J. Darensbourg, *Inorg. Chim. Acta*, **5**, 247 (1971).
(15) Anal. Calcd for $C_{16}H_{19}NO_5W$: C, 39.28; H, 3.91; N, 2.86; W, 37.58. Found: C, 39.14; H, 3.96; N, 2.83; W, 37.63.
(16) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **96**, 7808 (1974).
(17) E. O. Fischer and R. Aumann, *Chem. Ber.*, **102**, 1495 (1969).

Charles P. Casey,* Stanley W. Polichnowski
Ronald L. Anderson

Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received July 2, 1975

Steric Environment of the Active Center in Metathesis of Olefins

Sir:

Since the first disclosure of olefin metathesis by Calderon[1] many catalytic systems in the homogeneous phase have been reported.[2] The oxidation state of the metal (group 6a) in the precursor complex may vary from 0 to 6.

Activation of hexavalent (for tungsten) or pentavalent (for molybdenum) precursors is achieved by a great number of non-transition metal compounds such as $AlR_{3-n}Cl_n$.[1] (n-$C_4H_9)Li$,[3] $(CH_3)_4Sn$,[4] $(n$-$C_3H_7)MgBr$,[5] and $LiAlH_4$,[6] etc. With zerovalent precursor complexes, activation is usually obtained by means of Lewis acids.[7,8]

Due to this great variety of catalytic systems, the oxidation state as well as the coordination sphere of the active complex or complexes is unknown. We have therefore undertaken a stereochemical investigation of metathesis of *cis*-2-pentene with a great number of precursor complexes of tungsten; the purpose was to get information on the steric environment of the active catalyst or catalysts.

The major difficulty for such an approach is that metathesis of *cis*-2-pentene gives geometric isomerization of the products (2-butenes and 3-hexenes) and of the starting olefin. For highly active catalytic systems, cis-trans distribution of isomers reaches the equilibrium composition in a few minutes at room temperature. Concerning this geometric isomerization, several stereochemical studies have been reported on different systems such as: $WCl_6-C_2H_5AlCl_2-$
C_2H_5OH,[9] $W(CO)_5P(C_6H_5)_3-C_2H_5AlCl_2-O_2$,[10] L_2Mo-
$(NO)_2Cl_2-C_2H_5AlCl_2$.[11]

From the kinetics found for these reactions, we can take for granted the fact that cis-trans isomerization is a secondary reaction of metathesis which also proceeds by a metathetic mechanism. There are good reasons to assume that both reactions occur on the same active center. Thus, the only meaningful way to characterize the steric environment of the real catalyst in metathesis is to determine the stereoselectivity at 0% conversion.

The catalytic systems used in the present work were mainly zerovalent precursor complexes of tungsten associated with $C_2H_5AlCl_2$ and sometimes molecular oxygen. We also studied a catalytic system derived from hexavalent tungsten $(WCl_6-Sn(CH_3)_4)$. The solvent used was chlorobenzene in all cases. The results have been compared with various literature data related to hexavalent precursors of tungsten. In order to obtain a high accuracy concerning the trans/cis ratio of 2-butenes (C_4) and 3-hexenes (C_6) at 0% conversion, we have plotted these trans/cis ratios vs. the trans/cis ratio of 2-pentene. This gave us a linear relationship from which trans/cis C_4 and trans/cis C_6 ratios at 0% conversion have been deduced (Table I).

The fact that the same trans/cis ratios for C_4 and C_6 are obtained with all the catalytic systems used in the homogeneous phase is a very meaningful result; stereoselectivity of metathesis does not seem to depend: (1) on the electronic effects of the ligands coordinated to zerovalent precursor

Table I. Ratios (trans/cis) of 2-Butenes and (trans/cis) of 3-Hexenes for *cis*-2-Pentene Metathesis in Homogeneous Phase at 0% Conversion (at 25°C)

Catalysts[a]	Cocatalysts[a]	Trans/cis C_4[b]	Trans/cis C_6[b]
$W(CO)_6$	$C_2H_5AlCl_2$	0.69	
$W(CO)_5NH_2C_6H_{11}$		0.78	
$W(CO)_5P(n$-$C_4H_9)_3$		0.76	0.83
$W(CO)_5P(C_6H_5)_3$		0.73 ± 0.05[c]	0.88 ± 0.06[c]
$W(CO)_5P(OC_6H_5)_3$		0.76	0.89
$W(CO)_4(P(C_6H_5)_3)_2$-*trans*	$C_2H_5AlCl_2 + O_2$	0.77	
$W(CO)_4$(diphos)[d]	$C_2H_5AlCl_2$	0.72	
$W(CO)_3$(dien)[e]	$C_2H_5AlCl_2 + O_2$	0.69	
$W(CO)_3$(mesitylene)	$C_2H_5AlCl_2$	0.72	0.88
WCl_6[f]	$C_2H_5AlCl_2 + C_2H_5OH$	0.69	0.87
WCl_6	$Sn(CH_3)_4$[h]	0.73	
WCl_6[g]	$Li(n$-$C_4H_9)$	0.8 at 10% conversion	

[a] Experimental conditions: olefin/W = 100 and Al/W = 4. [b] Analysis of the gaseous phase for C_4 and of the liquid phase for C_6. [c] The uncertainty is deduced from the results of 25 experiments. [d] Diphos = bis(1,2-diphenylphosphino)ethane. [e] Dien = diethylentriamine. [f] Values obtained by plotting (trans/cis)C_4 vs. (trans/cis) C_6 from data of Calderon[9] (solvent:benzene). [g] Values obtained from data of Wang and Menapace[12] (solvent: benzene, n-pentane). [h] Sn/W = 1.

Table II. Ratios (trans/cis) of 2-Butenes for *cis*-2-Pentene Metathesis with Supported Complexes at 0% Conversion[a]

Catalyst	Carrier	Trans/cis C_4
$W(CO)_6$	$Al_2O_3\eta$	0.37 ± 0.05
$W(CO)_5P(n\text{-}C_4H_9)_3$		0.38
$W(CO)_5P(C_6H_5)_3$		0.38
$W(CO)_5P(OC_6H_5)_3$		0.40

[a] No reliable data were obtained with hexenes, due to a capillary condensation of C_6 on the catalyst.

complexes $W(CO)_5L$ (L = CO, P $(n\text{-}C_4H_9)_3$, P $(C_6H_5)_3$, P $(OC_6H_5)_3$, $NH_2C_6H_{11}$), (2) on the number of coordination sites (1–3) occupied by the ligands (L) in $W(CO)_5L$, $W(CO)_3L_3$, or on the steric hindrance of these ligands, (3) on the oxidation state of the precursor complexes (W^{6+}, W^0).

Some of the zerovalent precursor complexes have been deposited on an η alumina carrier. Metathesis of *cis*-2-pentene was carried out in the gaseous phase at 25°C. Results concerning stereoselectivity are given in Table II.

It is necessary to interpret these results by comparing homogeneous systems with heterogeneous ones. The fact that the stereoselectivity is modified upon interaction of the precursor complex with the surface of a solid indicates that this stereoselectivity depends on the steric environment of the transition metal.

Consequently steric results obtained in the pure homogeneous phase can supply valuable information on the steric effect of the ligand remaining coordinated to the active catalyst. It seems therefore that we have the same steric environment, whatever the precursor complex and the cocatalyst. That is, we have the same coordination sphere during the catalytic steps which govern stereochemistry of metathesis in all these cases. Tungsten has lost at least three ligands L; the complex $W(CO)_3$(arene) gives the same stereoselectivity as $W(CO)_6$. In fact tungsten has probably lost all its ligands L; $W(CO)_6$ and WCl_6 also exhibit the same stereoselectivity. Nevertheless this does not rule out the possibility of having one-electron ligands such as Cl, bonded to the active tungsten. It seems also that Al halide is not present on the active center since one obtains the same stereoselectivity with the catalytic systems WCl_6–$C_2H_5AlCl_2$–C_2H_5OH or WCl_6–$Sn(CH_3)_4$. This is corroborated by recent results of Dubois et al. concerning the photochemical activation of $W(CO)_6$ in a chlorine containing solvent.[13]

The results also seem to give an answer concerning the recent controversy about the homogeneous character of metathesis catalysts.[14] It now seems possible to make a clear distinction from a stereochemical point of view between homogeneous and heterogeneous systems. The two systems behave differently, and it seems that the homogeneous systems remain homogeneous in their active form at least with the precursor complexes used in the present work.

The rather weak stereoselectivity observed in the metathesis of acyclic olefins[15] neither supports nor refutes the mechanism of one carbene exchange proposed by Chauvin et al.[16,17] and verified later by others.[18–21]

This work does not seem to clarify the stereoselectivity aspect of metathesis of cyclic olefins. In the latter case about 90% cis or 90% trans polypentenamer can be observed[22–25] with cyclopentene depending on the experimental conditions. Although one could object than no precise stereochemical studies were performed with these systems at 0% conversion, the difference observed between metathesis of cyclic and acyclic olefins could be explained by the coordination to the catalyst of the first double bond after the carbene in the polymeric chain linked to the tungsten; evidently this cannot occur in the case of acyclic olefins
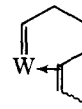
Finally it is worth mentioning that supported homogeneous catalysts exhibit a stereoselectivity which is quite different from that observed with pure homogeneous systems. Here we have evidence for the effect of the surface on the steric course of a catalytic reaction. This could represent one of the differences between homogeneous catalysis and catalysis by supported complexes.

References and Notes

(1) N. Calderon, H. Y. Chen, and K. W. Scott, *Tetrahedron Lett.*, 3327 (1967).
(2) W. B. Hughes, *Acc. Chem. Res.*, **5**, 127 (1972).
(3) J. L. Wang and H. R. Menapace, *J. Org. Chem.*, **33**, 3794 (1968).
(4) J. A. Moulijn and C. Boelhouwer, *Chem. Commun.*, 1170 (1971).
(5) P. A. Raven and E. J. Wharton, *Chem. Ind.* (*London*), 292 (1972).
(6) J. Chatt, R. J. Haines, and G. J. Leigh, *J. Chem. Soc., Chem. Commun.*, 1202 (1972).
(7) G. Doyle, *J. Catal.*, **30**, 118 (1973).
(8) J. M. Basset, G. Coudurier, R. Mutin, H. Praliaud, and Y. Trambouze, *J. Catal.*, **34**, 196 (1974).
(9) N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, *J. Am. Chem. Soc.*, **90**, 4133 (1968).
(10) J. M. Basset, G. Coudurier, R. Mutin, and H. Praliaud, *J. Catal.*, **34**, 152 (1974).
(11) W. B. Hughes, *Chem. Commun.*, 431 (1969).
(12) J. L. Wang, H. R. Menapace, and M. Brown, *J. Catal.*, **26**, 455 (1972).
(13) P. Frausz, F. Garnier, and J. E. Dubois, *J. Am. Chem. Soc.*, **97**, 437 (1975).
(14) E. L. Muetterties and M. A. Busch, *J. Chem. Soc., Chem. Commun.*, 754 (1974).
(15) The nature of the geometric isomer also seems to be a determining factor; when starting from *trans*-2-pentene with the zerovalent complexes $W(CO)_5P(C_6H_5)_3$ or $W(CO)_3$(arene) associated to the system $C_2H_5AlCl_2$ + O_2, no metathesis occurs, whereas introduction of small amounts of *cis*-2-pentene initiates the reaction. Steric effects are therefore of great importance in the formation of the tungsten carbene moiety responsible for initiation of the chain reaction.
(16) J. L. Herisson and Y. Chauvin, *Makromol. Chem.*, **141**, 161 (1970).
(17) J. P. Soufflet, D. Commereuc, and Y. Chauvin, *C.R. Acad. Sci., Ser. C*, **276**, 169 (1973).
(18) T. J. Katz and J. Mc Ginnis, *J. Am. Chem. Soc.*, **97**, 1592 (1975).
(19) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **96**, 7808 (1974).
(20) R. H. Grubbs, P. L. Burk, and D. D. Carr, *J. Am. Chem. Soc.*, **97**, 3265 (1975).
(21) E. L. Muetterties, *Inorg. Chem.*, **14**, 951 (1975).
(22) G. Natta, G. Dall'asta, and C. Mazzanti, *Angew. Chem.*, **76**, 765 (1964).
(23) P. Günther, F. Haas, G. Marwede, K. Nützel, W. Oberkirch, G. Pampus, N. Schön, and J. Witte, *Angew. Makromol. Chem.*, **14**, 87 (1970).
(24) R. J. Minchak and H. Tucker, *Polym. Repr., Am. Chem. Soc., Div. Polym. Chem.*, **13**, No. 2, 885 (1972).
(25) Private communication of N. Calderon.

J. M. Basset,* J. L. Bilhou, R. Mutin, A. Theolier

*Institut de Recherches sur la Catalyse
69626 Villeurbanne, France*

Received August 13, 1975

Steric Acceleration in Alkyldiazene (Azoalkane) Decompositions. Evidence for a Concerted Mechanism

Sir:

A number of techniques have been used to support either a concerted (two-bond, eq 1) or nonconcerted (one-bond, eq 2) mechanism for the thermal decomposition of dialkyl- and alkylaryldiazenes. These studies, which include CIDNP observations of diazenyl radicals;[1] effect of pressure,[2] solvent viscosity,[3] and structure[4] on decomposition rate; racemization of chiral diazenes;[5] intramolecular trapping of diazenyl radicals;[6] kinetic isotope effects;[7] and thermochemical considerations,[8] do not show total unanimity of thought.[1–8] However, most of the data can be accommodated by eq 1